JANUARY - MARCH • 1954

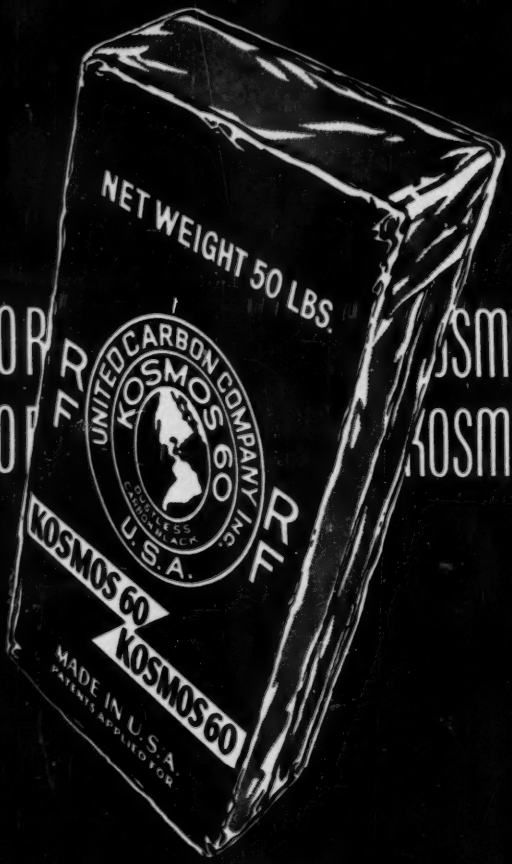
VOLUME XXVII • NUMBER ONE

RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED QUARTERLY BY THE
DIVISION OF RUBBER CHEMISTRY
OF THE AMERICAN CHEMICAL SOCIETY

KOSMOS 60 RF KOSMOS 60 RF

KOSMOS 60 RF KOSMOS 60 RF



Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil and is perfected by United's exclusive process. Its superb processing and balance of strength make for the best in rubber products.

UNITED CARBON COMPANY, INC.

CHARLESTON 27, W. VA.

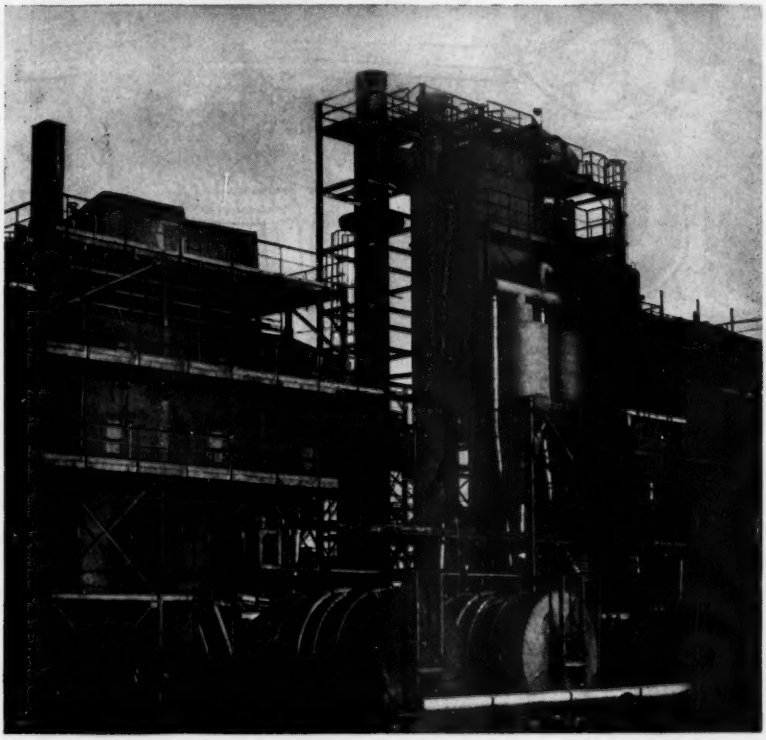
NEW YORK • AKRON • CHICAGO • BOSTON

CANADA: CANADIAN INDUSTRIES LIMITED

WITCO-CONTINENTAL'S

new facilities at Sunray—where CONTINEX® SRF, HMF and FEF Blacks are now in expanding production to meet your growing demands.

#3 unit at Sunray, Texas, showing bag filter, cyclone collector and pelletizing drums.



WITCO CHEMICAL COMPANY

CONTINENTAL CARBON COMPANY

260 Madison Avenue • New York 16, N. Y.

Akron • Amarillo • Los Angeles • Boston • Chicago • Houston
Cleveland • San Francisco • London and Manchester, England

Entered as second-class matter March 19, 1943, at the Post Office at Lancaster, Pa., under the Act of August 24, 1912. Acceptance for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. and R. of 1948, authorized September 25, 1940.

For Tires, or Belts, or Rubber Shoes
There's a PHILBLACK* you should use!

For better extruded or molded products, use PHILBLACK A, easy-mixing, easy-processing FEF (Fast Extrusion Furnace) black.

For improved abrasion resistance and long flex life, try PHILBLACK O, HAF (High Abrasion Furnace) black.

For extra long wear at moderate cost, use PHILBLACK I, popular new ISAF (Intermediate Super Abrasion Furnace) black.

For super durability—PHILBLACK E. This SAF (Super Abrasion Furnace) black is the toughest black on the market! Extreme abrasion resistance!

For full information consult our technical sales representative or write our nearest office.

PHILLIPS CHEMICAL COMPANY

PHILBLACK SALES DIVISION

318 WATER STREET • AKRON 8, OHIO

PHILBLACK EXPORT SALES DIVISION

80 BROADWAY • NEW YORK 5, N. Y.

The Philblacks are manufactured at Borger, Texas.
Warehouses in Akron, Boston, Chicago, and Trenton.
West Coast agent: Harwick Standard Chemical Company, Los Angeles.
Canadian agent: H. L. Blachford, Ltd., Montreal and Toronto.

*A Trademark

TIME-TESTED VERSATILE

SHARPLES ACCELERATOR

52

TETRAMETHYL-THIURAM DISULFIDE

Natural Rubber **Nitrile Rubber** **GR-S**	For HEAT RESISTANCE—SUPER AGING—TARNISH RESISTANCE Use 3.0-4.0 PHR of **SA 52** as the VULCANIZING AGENT. For FAST, TIGHT CURE Use 0.4-1.5 PHR of **SA 52** as PRIMARY ACCELERATOR with 1.0-2.5 PHR of sulfur. To ACTIVATE THIAZOLES Use 0.05-0.30 PHR of **SA 52** as a SECONDARY ACCELERATOR.
Butyl Rubber	For STANDARD ACCELERATION Use 1.0-3.0 PHR of **SA 52** with 0.5-2.0 PHR of sulfur. For HEAT RESISTANCE—TARNISH RESISTANCE Use 3.0-4.0 PHR of **SA 52** as the VULCANIZING AGENT.
Neoprene GN	To INCREASE SCORCH TIME Use 1.0-2.0 of **SA 52**.

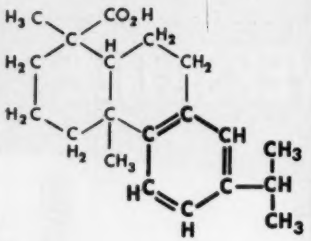
SHARPLES TRADE MARK CHEMICALS

SHARPLES CHEMICALS INC.

Fifth Ave., New York • 80 E. Jackson Blvd., Chicago • 106 S. Main St., Akron
West Coast: Los Angeles • Berkeley • Portland • Tacoma
Shawinigan Chemicals, Ltd., Montreal • Toronto
Alco Company International, New York

GALEX®

A superior tackifier and plasticizer for GR-S, NEOPRENE, NATURAL RUBBER and RECLAIM



FORMULA

"Galex" is a stable rosin acid that effectively tackifies and plasticizes GR-S, Neoprene, natural rubber and reclaim. Because of its chemical structure, principally dehydroabietic acid, "Galex" is unaffected by oxidative aging. It is compatible with various elastomers, resins and solvents.

"Galex" is widely used as a tackifier-plasticizer in hose, belting, mechanical goods and various friction stocks. It imparts strong surface tack which develops into excellent adhesion after cure. "Galex" also functions as a highly stable and compatible tackifier in rubber-base adhesives and cements.

"Galex" may be the tackifier-plasticizer you need to build maximum quality into *your* compound. Its superior tack, excellent aging resistance and high compatibility warrant your investigation. Write for technical information and samples.

Thiokol Chemical Corporation

784 NORTH CLINTON AVENUE • TRENTON 7, NEW JERSEY

In Canada: Naugatuck Chemicals Division, Dominion Rubber Company, Elmira, Ontario

NEWS IN NITRILES—

the light color, light bale of CHEMIGUM

NEWEST of the nitrile rubbers are CHEMIGUM N-6 and CHEMIGUM N-7. They are the same basic polymers as the other CHEMIGUM rubbers. But they have the added advantages of a much lighter—almost white color—and a much lighter—50 pound—bale.

The new color offers new possibilities in compounding. The new bale means easier handling without excessive handling. With these new features, CHEMIGUM now gives you all you desire in a nitrile rubber – service, uniformity, ease of handling and processing, outstanding oil resistance and excellent physical properties.

For full details on the new CHEMIGUM N-6 or N-7, write to:

Goodyear, Chemical Division, Akron 16, Ohio

We think you'll like "THE GREATEST STORY EVER TOLD" every Sunday—ABC Radio Network THE GOODYEAR TELEVISION PLAYHOUSE every other Sunday—NBC TV Network

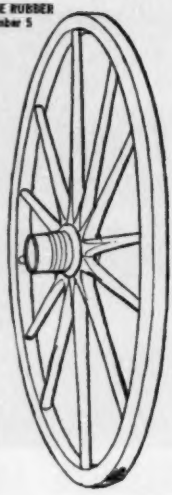
CHEMICAL GOODYEAR DIVISION

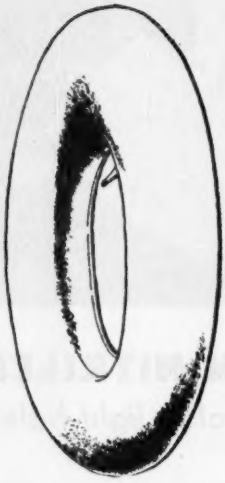
Chemigum, Pliobond, Pliolite, Plio-Tuf, Pliovic —T. M.'s The Goodyear Tire & Rubber Company, Akron, Ohio

Use-Proved Products — CHEMIGUM · PLIOBOND · PLIOLITE · PLIO-TUF · PLIOVIC · WING-CHEMICALS — The Finest Chemicals for Industry

THE HISTORY OF THE RUBBER INDUSTRY— Number 5

how long did it take to get from here to here?





Answer: Two years.

The principle of an inner tube is simple, and of such ancient application that it could not be patented.

Inner tubes, as we think of them today, were probably used about 1890. By 1892—two years later—they were being used widely, and beginning to appear as the detachable tube, for double tube tires, and the vulcanized-in type, used in single tube tires.

Two Monsanto accelerators, Thiofide (powder) and Thiofide S (seeds), can be used successfully in a wide variety of stocks. The seeds give maximum speed and completeness of dispersion. For more information about these accelerators and other products, see catalog "Monsanto Chemicals for the Rubber Industry." If you do not have a copy, write to MONSANTO CHEMICAL COMPANY, Rubber Service Department, 920 Brown Street, Akron 11, Ohio.

Monsanto Chemicals For the Rubber Industry

ANTIOXIDANTS
Flectol* H
Santoflex* B
Santoflex BX
Santoflex 35
Santoflex AW
Santowhite* Crystals
Santowhite MK
Santowhite L

ALDEHYDE AMINE ACCELERATORS
A-32
A-100

MERCAPTO ACCELERATORS
Santocure*
El-Sixty*
Mertax (Purified Thiotax)
Thiotax (2-Mercapto benzothiazole)
Thiofide* (2,2' dithio-bis benzothiazole)

GUANIDINE ACCELERATORS
Diphenylguanidine (D.P.G.)
Guantal*

ULTRA ACCELERATORS FOR LATEX, ETC.
R-2 Crystals
RZ-50
RZ-50-B
Pip-Pip
Thiurad* (Tetramethylthiuram disulfide)
Ethyl Thiurad (Tetraethylthiuram disulfide)
Mono Thiurad (Tetramethylthiuram monosulfide)
Methasan* (Zinc salt of dimethyl dithiocarbamic acid)
Ethasan* (Zinc salt of diethyl dithiocarbamic acid)
Butasan* (Zinc salt of dibutyl dithiocarbamic acid)

SPECIAL MATERIALS
Thiocarbanilide ("A-1")
Santovar*-A
Santovar-O
Sulfasan R
Insoluble Sulfur "60"

COLORS

REODORANTS

**Reg. U. S. Pat. Off.*

MONSANTO
CHEMICALS – PLASTICS
SERVING INDUSTRY... WHICH SERVES MANKIND

...the law

One fundamental law of economics specifies ... for a successful operation always be assured adequate supplies of top-quality raw materials at competitive prices.

The Sid Richardson Carbon Co. meets the spirit and letter of this law for its customers with:

1. Its own nearby natural resources to assure continuous supply
2. Plant separated into individual units to make specification products
3. Economical to use channel blacks

For continued success use ***TEXAS "E"*** or ***TEXAS "M"*** channel blacks.

TEXAS CHANNEL BLACKS

Sid Richardson
CARBON CO.
FORT WORTH, TEXAS

GENERAL SALES OFFICES
EVANS SAVINGS AND LOAN BUILDING
AKRON 8, OHIO

Look at...
HYDROCARBON
PANAREZ
RESINS
AS A
QUALITY
ECONOMICAL RESIN
IN RUBBER COMPOUNDING
PANAREZ hydrocarbon resins are effective and inexpensive for rubber compounding. They have low specific gravity · Low odor · Show no effect on cure · There is a marked improvement in processing · Longer flex life · Greater abrasion resistance · Better color stability · Electrical characteristics are excellent.
Prompt shipments made in carload or single drum quantities.
Write for samples.

	Color Gardner	Softening Point, °F	Specific Gravity	Acid Number
PANAREZ 3-210	9	200-220	1.049	0-1
PANAREZ 6-210	11	200-220	1.106	0-1
PANAREZ 12-210	16	200-220	1.054	0-1

PAN AMERICAN CHEMICALS

PAN AMERICAN Chemicals
DIVISION
Pan American Refining Corp.
122 EAST 42ND STREET · NEW YORK 17, N. Y.

CABOT AS THE WORLD'S ONLY CARBON BLACK MANUFACTURER OF CHANNEL, FURNACE AND THERMAL GRADES

offers the greatest variety of

NON-STAINING CARBON BLACKS

available to the rubber industry

CABOT'S NON-STAINING CARBON BLACKS		
STERLING SO	FEF	Fast Extruding Furnace
STERLING V Non-Staining	GPF	General Purpose Furnace
STERLING NS	SRF	Semi-Reinforcing Furnace
PELLETEX NS	SRF	Semi-Reinforcing Furnace
STERLING MT Non-Staining	MT	Medium Thermal

AND, although Vulcan 3 HAF (High Abrasion Furnace), Vulcan 6 ISAF (Intermediate Super-Abrasion Furnace), and Vulcan 9 SAF (Super-Abrasion Furnace) carbon blacks made from oil are used primarily for their high reinforcement properties, they also possess non-staining characteristics.

GODFREY L. CABOT, INC.
77 FRANKLIN ST., BOSTON 10, MASS.

CABOT

KOPPERS CHEMICALS...

Staples in the rubber industry

whitewall tires

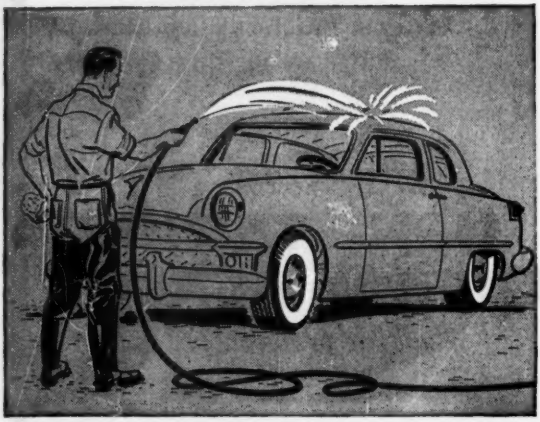
rubber hose

rubber boots

rubber molding

rubber automotive components

grommets, hoses, cushions



STYRENE MONOMER may be polymerized with other active olefinic materials to produce a variety of synthetic rubbers and resins having a wide range of desirable properties. Koppers controls its own raw materials for the production of styrene, thus assuring continuity of supply.

RESORCINOL is used for both the preparation of adhesives that assure strong bonds between rubber or synthetic rubber and nylon, rayon and cotton tire cords and the manufacture of conveyor belts, hose, etc.

Di-tert-BUTYL-para-CRESOL has application as an antioxidant in white rubber products. It retards cracking, hardening and loss of strength without discoloring the product or staining materials with which the product comes in contact.

DIVINYLBENZENE (20-25% and 50-60% grades) in synthetic rubber manufacture improves processing and decreases shrinkage of the product. With styrene and other monomers, it produces insoluble and infusible copolymers.

MONO-tert-BUTYL-meta-CRESOL is used in the manufacture of an effective anti-flex cracking agent for rubber and rubber-like materials. The resin obtained by condensation of MBMC with formaldehyde imparts tack to GR-S rubber. For detailed information on any of these products, please write to:

KOPPERS COMPANY, INC.

Chemical Division, Dept. RA-34, Pittsburgh 19, Pennsylvania

KOPPERS®

Koppers Chemicals

SALES OFFICES: NEW YORK · BOSTON · PHILADELPHIA
ATLANTA · CHICAGO · DETROIT · LOS ANGELES

chemicals for the rubber industry

ACCELERATORS

Thiazole

MBT (Mercaptobenzothiazole)
MBT-XXX (Specially Refined—Odorless)
MBTS (Benzothiazyldisulfide)
NOBS* No. 1 Accelerator
NOBS* SPECIAL Accelerator

Guanidine

DPG (Diphenylguanidine)
DOTG (Diorthotolylguanidine)
Accelerator 49

ANTIOXIDANT

Antioxidant 2246*
(Non-staining, non-discoloring type)

PEPTIZER

Pepton® 22 Plasticizer

RETARDER

Retarder P.D.

SULFUR

Rubber Makers' Grade

*Trade-mark

AMERICAN Cyanamid COMPANY Calco®

INTERMEDIATE & RUBBER CHEMICALS DEPARTMENT
BOUND BROOK, NEW JERSEY, U.S.A.

SALES REPRESENTATIVES AND WAREHOUSE STOCKS: Akron Chemical Company, Akron, Ohio • Ernest Jacoby and Company, Boston, Mass. • Herron & Meyer of Chicago, Chicago, Ill. • H. M. Royal, Inc., Los Angeles, Calif. • H. M. Royal, Inc., Trenton, N. J. • In Canada: St. Lawrence Chemical Company, Ltd., Montreal and Toronto

announcing
a change in name
FROM
THE NEVILLE COMPANY
TO
NEVILLE CHEMICAL COMPANY
To more aptly relate our corporate name to the ever-growing field which we have served through the years, and to more readily identify the scope of our products and service, we have changed our name.
Needless to say, only the name has been changed, and we hope the new name will come to symbolize the same high standard of quality that has characterized the old throughout the industry.
NEVILLE
PRODUCTS OF TOMORROW
FROM THE CHEMICALS OF TODAY
NEVILLE CHEMICAL CO.
PITTSBURGH 25, PA.
Plants at Neville Island, Pa., and Anaheim, Cal.

Looking for
the finest in...

rubber chemicals?
Try Naugatuck

PROCESS...ACCELERATE...PROTECT

NAUGATUCK offers a complete line of proven accelerators, activators, antioxidants, and special chemicals to give you thorough control of rubber product manufacture and performance.

ACCELERATORS

Thiazoles—M-B-T • M-B-T-S • O-X-A-F
Thiurams—MONEX* • MORFEX
PENTEX* • TUEX • ETHYL TUEX
Dithiocarbamates—ARAZATE*
BUTAZATE* • ETHAZATE*
METHAZATE*
Aldehyde Amines—BEUTENE*
HEPTEEN* • HEPTEEN BASE*
TRIMENE* • TRIMENE BASE*
Xanthates—C-P-B* • Z-B-X*

(MONEX, TUEX, ETHYL TUEX, METHAZATE, and ETHAZATE are furnished either in powder form or in fast-dispersing, free-flowing NAUGETS.)

ACTIVATORS

D-B-A • G-M-F • DIBENZO G-M-F
VULKLOR

ANTIOXIDANTS

AMINOX* • ARANOX*
BETANOX* SPECIAL • B-L-E*
B-X-A • FLEXAMINE • V-G-B*
OCTAMINE*

SPECIAL PRODUCTS

BWH-1 • CELOGEN • E-S-E-N
LAUREX* • SUNPROOF*-713
SUNPROOF* IMPROVED
SUNPROOF* JUNIOR
TONOX* • KRALAC* A-EP

SPECIAL PRODUCTS FOR SYNTHETIC POLYMERS

POLYGARD—stabilizer
THIOSTOP K & N—short stops

*Reg. U. S. Pat. Office.

Write, on your letterhead, for technical data or assistance with any Naugatuck product

Naugatuck Chemical

Division of UNITED STATES RUBBER COMPANY
551 Elm St., Naugatuck, Conn.
IN CANADA: NAUGATUCK CHEMICALS DIVISION
Dominion Rubber Company, Limited, Elmira, Ontario
Rubber Chemicals • Aromatics • Synthetic Rubber • Plastics • Agricultural Chemicals
Reclaimed Rubber • Latices

HERE'S EXPERIENCE THAT CAN HELP YOU WITH YOUR PROCESSING

When you need a process aid or have a problem involving one, it will pay you to take advantage of Sun's technical knowledge and experience in the field.

As early as 1937, working with leading rubber companies, Sun made commercially available a petroleum derivative remarkably suited for plasticizing Neoprenes, natural rubbers and reclaims. This was followed by a number of other process aids—among them Circosol-2XH, an elasticator that greatly improved the rebound properties of GR-S synthetics; and Sundex-53, a low-cost product highly compatible with natural rubbers, GR-S, reclaims, and various combinations of the three. Leadership in the field and knowledge of the industry's requirements brought about Sun's participation in the work which led to the development of oil-extended synthetic rubbers.

Put this experience, plus a complete line of products, to work for you—in lowering costs, in improving product quality, in solving processing problems. For the assistance of Sun's technologists, write Dept. RC-1.

INDUSTRIAL PRODUCTS DEPARTMENT

SUN OIL COMPANY SUNOCO®

PHILADELPHIA 3, PA. • SUN OIL COMPANY LTD., TORONTO & MONTREAL

RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXVII NUMBER 1

January-March, 1954

Published under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

CARBON BLACKS

for **RUBBER COMPOUNDING**

SAF (Super Abrasion Furnace)
STATEX® 125

HAF (High Abrasion Furnace)
STATEX-R

MPC (Medium Processing Channel)
STANDARD MICRONEX®

EPC (Easy Processing Channel)
MICRONEX W-6

FF (Fine Furnace)
STATEX-B

FEF (Fast Extruding Furnace)
STATEX-M

HMF (High Modulus Furnace)
STATEX-93

SRF (Semi-Reinforcing Furnace)
FURNEX®

• COLUMBIAN COLLOIDS •

COLUMBIAN CARBON CO. MANUFACTURER • **BINNEY & SMITH INC.** DISTRIBUTOR

500 TONS OF SMOKE A DAY

RUBBER CHEMISTRY AND TECHNOLOGY

Published Quarterly under the Auspices of the Division of Rubber Chemistry of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

Editor ..... C. C. DAVIS
Advertising Manager ..... E. H. KRISMANN
Secretary ..... A. M. NEAL
Treasurer ..... A. W. OAKLEAF

Vol. XXVII **January–March, 1954** **No. 1**

CONTENTS

General Section PAGE

Officers iii
New Books and Other Publications iii

Papers

The Structure of the System: Filler Rubber. An Electron-Microscopic Study. FRIEDRICH ENDTER 1
Vitrification of High Polymers in Periodic Deformation. G. M. BARTENEV 12
Plasticity and Filler Structure in Carbon Black Stocks. R. W. WHORLOW 16
Rheology of Unmasticated and Masticated Smoked Sheet. R. W. WHORLOW 20
Relaxation Time Spectrum, Elasticity, and Viscosity of Rubber. I. W. KUHN, O. KÜNZLE, AND A. PREISSMANN 36
Relaxation Time Spectrum, Elasticity, and Viscosity of Rubber. II. W. KUHN, O. KÜNZLE, AND A. PREISSMANN 54
Hydrogenated Synthetic Elastomers. R. VERNON JONES, C. WAYNE MOBERLY, AND W. B. REYNOLDS 74
Diazo-Initiated Polymers. Preparation, Properties, and Evaluation. J. M. WILLIS, GLEN ALLIGER, B. L. JOHNSON, AND W. M. OTTO 88
Yield Stress in Frozen Rubbers. J. M. BUIST AND R. L. STAFFORD 104
Effect of Temperature on Rate of Oxidation of Rubber. Nature of Resultant Deterioration. J. REID SHELTON, FRED J. WHERLEY, AND WILLIAM L. COX 120
Mercaptobenzothiazole Vulcanization Using Sulfur.[25] IRVING AUERBACH 134
Acceleration and Aging. ADRIEN HAEHL 147
A Study of the Mechanism of the Deactivation Effect. JACQUES LE FOLL 157
Equilibrium Between Rubber and Alcohol-Benzene Solutions. G. L. STAROBINETS AND V. S. KOMAROV 165
Ozone Cracking. A Cinematographic Study. DOREEN M. SMITH AND V. E. GOUGH 175

Ozone Formation in Photochemical Oxidation of Organic Substances. A. J. Haagen-Smit and C. E. Bradley 192
Calculable Properties of Technical Rubber Mixtures. E. Schreuer 201
Nonlinearity in the Dynamic Properties of Vulcanized Rubber Compounds. W. P. Fletcher and A. N. Gent 209
Factors Affecting the Measurement of Strain. L. L. Best 223
The Velocity and Temperature Dependence of Rubber Friction. A. Schallamach. 234
Notes on the Use of Plasticity Tests to Assess Scorching of Rubber Stocks. R. W. Whorlow 242
Comparison of Rotation, Extrusion, and Compression Plastometers. R. W. Whorlow 248
Study of the Factors Affecting the Friction of Tread Compounds on Ice. C. S. Wilkinson, Jr. 255
Plasticization of Rubber in the Form of Latex. Marc Conté 271
Titer Compounding of Neoprene Latex. G. S. Cook and J. C. Fitch 277
Zinc Soap Formation and the Gelling of Latex. J. L. M. Newnham 286
Fractions from Hevea Brasiliensis Latex Centrifuged at 59,000 g. A. S. Cook and B. C. Sekhar 297
Tensile Properties of Films from Low-Temperature GR-S Latex. R. W. Brown, W. E. Messer, and L. H. Howland 302

RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues ($4.00 per year) to the Division and thus receive Rubber Chemistry and Technology.

(2) Anyone who is not a member of the American Chemical Society may become an Associate of the Division of Rubber Chemistry upon payment of $6.50 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive Rubber Chemistry and Technology.

(3) Companies and libraries may subscribe to Rubber Chemistry and Technology at the subscription price of $7.50 per year.

To these charges of $4.00 and $7.50, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications to become Members or Associates of the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, A. W. Oakleaf, Phillips Chemical Co., 318 Water St., Akron 8, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY

OFFICERS AND EXECUTIVE COMMITTEE

Chairman·····J. C. WALTON, Boston Woven Hose & Rubber Co., Cambridge, Mass.

Vice-Chairman·····J. M. BALL, R.F.D. No. 1, Millstone Rd., Wilton, Conn.

Secretary·····A. M. NEAL, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

Treasurer·····A. W. OAKLEAF, Phillips Chemical Co., Akron, Ohio

Editor of *Rubber Chemistry and Technology*····C. C. DAVIS, Boston Woven Hose & Rubber Co., Cambridge, Mass.

Advertising Manager of *Rubber Chemistry and Technology*····E. H. KRISMANN, E. I. du Pont de Nemours & Co., Inc., Akron, Ohio

Directors····S. G. BYAM (Past Chairman), G. R. CUTHBERTSON (Director-at-Large), C. A. RITCHIE (Akon), H. L. HAAS (Boston), C. O. MISERINTINO (Buffalo), A. E. LAURENCE (Chicago), G. R. SPRAGUE (Connecticut), W. J. SIMPSON (Detroit), S. M. YORAN (Fort Wayne), G. W. MILLER (Los Angeles), G. N. VACCA (New York), R. D. FORD (Northern California), T. W. ELKIN (Philadelphia), F. W. BURGER (Rhode Island), J. R. WALL (Southern Ohio), R. E. HARMON (Washington, D. C.).

Councillors····A. M. Neal, 1951–4, W. L. SEMON, 1952–5 (Alternates, J. H. FIELDING, 1951–4, H. I. CRAMER, 1952–5).

NEW BOOKS AND OTHER PUBLICATIONS

SYMPOSIUM ON CONDITIONING AND WEATHERING. (Technical Publication No. 133.) Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 104 pp. Heavy Paper Cover. $2.25.—A Symposium on Conditioning and Weathering was held during the 1952 Annual Meeting of the Society under the sponsorship of Committee E-1 on Methods of Testing. Ten papers were presented, covering a variety of materials which are affected to some extent by atmospheric influences. All the papers, as well as subsequent discussion, are reproduced in this booklet. Among specific materials covered by the papers are textiles, paper, adhesives, plastics, organic coatings, and metallic coatings. Other papers are devoted to fundamentals of atmospheric elements, air conditioning for the laboratory, moisture resistance tests, outdoor exposure testing on racks and test fences, and accelerated weathering devices. An introduction to the symposium by Robert Burns of the Bell Telephone Laboratories, who presided over the session, is also included. [From *The Rubber Age* of New York.]

MIRACLES OF RESEARCH. Goodyear Tire & Rubber Co., Akron 16, Ohio. 6 × 9 in. 48 pp.—This interesting booklet marks the 10th anniversary of the Goodyear Research Laboratory, and reviews the accomplishments of this

laboratory during the past ten years. The manner in which the laboratory contributed to the development of synthetic rubber is recounted, and continuing work on "cold rubber", oil-enriched rubber and the new polyester rubber is discussed. Also covered is the work the laboratory has been doing in textile research, vinyls, chemicals, and in end-products for home and industry. Illustrated with photographs, the booklet covers a particularly interesting portion of the history of rubber in that the period discussed includes the developments of World War II and the Korean conflict. [From *The Rubber Age* of New York.]

STANDARDS OF ELECTRICAL INSULATION MATERIALS: 1953. Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 590 pp. Heavy Paper Cover. $5.25.—The 1953 edition of this compilation, prepared by ASTM Committee D-9 on Electrical Insulating Materials, contains in their latest approved form 75 widely used ASTM standards, including 56 test methods, 16 specifications, 2 recommended practices, and a list of definitions, with procedures relating to conditioning and weathering. Among products covered by the standards are rubber tape and electrical protective equipment, insulating fabrics, plastics for electrical insulation, and insulating shellac and varnish. Appendexes cover the significance of tests of electrical insulating materials and proposed recommendations for writing statements as to the usefulness of tests of such materials. An innovation in the 1953 edition is the use of Bible paper, which provides a substantial reduction in bulk of the book, making it a compact volume of convenient size. [From *The Rubber Age* of New York.]

CHEMISTRY OF CARBON COMPOUNDS. Volume II, Part A: Alicyclic Compounds. Edited by E. H. Rodd, Elsevier Publishing Co., 402 Lovett Blvd., Houston, Tex. Cloth, 6 by 9 inches, 510 pages. Price, $12.50.—This second of a five-volume set covers the chemistry of nonaromatic carbocyclic compounds and is divided into two parts, of which this is the first. This book consists of 11 chapters. The first is an introduction to the subject; while the other chapters are devoted to the chemistry of alicyclic compounds of increasing complexity. The first nine chapters, contributed by R. A. Raphael, cover the following topics: introduction; cyclopropane group; cyclobutane group; cyclopentane group; cyclohexane group; cycloheptane, cyclo-octane, and macrocyclic groups; polynuclear alicyclic compounds with separate ring systems and spiro compounds; polynuclear alicyclic compounds with condensed cyclic systems; and bridged ring systems. The remaining chapters and their contributors are: "The Carotenoid Group", R. F. Hunter; and "Open-Chain and Cyclic Polymers Derived from Olefinic Compounds; Rubber and Rubber like Compounds, Natural and Synthetic, and Their Derivatives," by R. G. R. Bacon. Features of the book are the many literature references given throughout the text, and the comprehensive subject index. [From the *India Rubber World.*]

ORGANIC ANALYSIS. Volume I. Edited by John Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer, and A. Weissberger. Interscience Publishers, Inc., 250 Fifth Ave., New York 1, N. Y. Cloth, 6 by 9 inches, 481 pages. Price, $8.50.—This is the first volume of a new series to cover the field of organic quantitative nonelemental analysis, a subject usually covered inadequately in the formal education of industrial organic and analytical chemists. Prepared

with the assistance of an advisory board of 22 specialists in the field, the series will present a review of current knowledge of non-elemental analysis and critical evaluations of the procedures employed.

This first volume, dealing with functional group analysis, consists of nine contributed chapters: "Determination of Hydroxyl Groups", V. C. Mehlenbacher; "Determination of Alkoxyl Groups", A. Elek; "Determination of the Alpha-Epoxy Group", J. L. Jungnickel, E. D. Peters, A. Polgar, F. T. Weiss; "Organometallic Compounds for the Determination of Active Hydrogen", G. F. Wright; "Diazomethane for the Determination of Active Hydrogen", F. G. Arndt; "Determination of Carbonyl Compounds" and "Determination of Acetals", Mitchell; "Determination of Organic Sulfur Groups", S. D. Nogare; and "Spectroscopic Functional Group Analysis in the Petroleum Industry", N. D. Coggeshall. [From the *India Rubber World.*]

SYMPOSIUM ON PLASTICS TESTING—PRESENT AND FUTURE. (Special Technical Publication No. 132.) Published by the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6 × 9 in. 76 pp. $2.00.—Papers which were presented at the symposium on "Plastics Testing—Present and Future", in June, 1952, at the meeting of ASTM Committee D-20 on Plastics are assembled in this publication. A wide range of topics is covered, as is indicated by the paper titles: "The Measurement and Significance of the Mechanical Strength Properties of Plastics"; Measurement of the Effect of Temperature on Some Physical Properties of Plastics"; "Measurement of Color, Gloss and Haze"; "The Effects of Molding Conditions on the Permanence of Plastics", and "Residual Stresses in Phenolic Plastics". The papers are complete with references and bibliographies. In addition, the discussions which followed the presentation of the papers also appear. [From *The Rubber Age* of New York.]

THE HANDBOOK OF SOLVENTS. By Leopold Scheflan and Morris Jacobs. Published by D. Van Nostrand Co., Inc., 250 Fourth Ave., New York 3, N. Y. 6½ × 9½ in. 728 pp. $10.00.—This comprehensive handbook covers various theoretical and practical attributes of solvents, solvent recovery, and the physical properties of over 2700 liquid organic compounds, arranged under multiple headings for quick and positive reference. The first portion of the book covers such theoretical and practical aspects as solvent action, solvent power, vapor pressure, evaporation rates, dilution rates, the limits of inflammability and safe practices in the use of solvents. Solvent recovery, of direct interest to the rubber field, is discussed in considerable detail, with much helpful bibliographical material. The second portion consists of a survey of the "constants" of commercial solvents as sold, and data on substances which may become important commercial solvents in the future. Not only can "actual constants" be located, but information also may be found under compound name and by synonym. Included are data on formula, weight, melting point, range, viscosity, surface tension, etc. The solubility of water in solvents and solvents in water is contained in a special section. Adding to the value of the handbook is the inclusion of a number of tables, and index of synonyms, and a general index. This new handbook is a most useful contribution to the literature of solvents. [From *The Rubber Age* of New York.]

CHEMICAL PROCESS MACHINERY. Second Edition. Emil Raymond Riegel Reinhold Publishing Corp., 330 W. 42nd St., New York 36, N. Y. Cloth, 6 by 9 inches, 742 pages. Price, $12.50.—This revised and greatly expanded edition of Riegel's highly regarded book presents up-to-date information on equipment used in the chemical and process industries in terms understandable to engineers, students, and laymen. Covering only equipment available commercially, this edition embraces the latest developments in machinery; has new material on distillation, mixing, and instrumentation; gives enlarged descriptions of evaporators, dryers, heaters, coolers, pumps, and other machinery; and has eliminated material on equipment which is now obsolete.

Classification of equipment is by function, and the chapters deal with plant-site selection; size reduction, screening and grading; conveying and elevating; tanks and containers; pumps; weighing and proportioning; gas propulsion; gas cleaning; mixing; separators; evaporators; crystallizers; dryers; distillation; vacuum equipment; heat exchangers; heaters and coolers; gas conditioning; hydraulic equipment; high-pressure equipment; and instrumentation. An appendix of reference data and a comprehensive subject index are also included in the book. [From the *India Rubber World.*]

THE STRUCTURE OF THE SYSTEM: FILLER RUBBER. AN ELECTRON-MICROSCOPIC STUDY *

FRIEDRICH ENDTER

CARBON BLACK LABORATORY OF THE DEUTSCHE GOLD- UND SILBERSCHEIDEANSTALT, WERK KALSCHEUREN, GERMANY

It has long been known that the incorporation of certain pigments of very small particle size in rubber converts a portion of the latter into a form insoluble in benzene. Le Blanc, Kröger, and Kloz[1] attributed this phenomenon to adsorption of part of the rubber on the surface of the filler. Fielding[2] coined the expression *bound rubber* for this benzene-insoluble component.

During the last few years, the formation of bound rubber with respect to its dependence on the properties of the fillers, time and temperature of mixing, time of storage, and subsequent heat treatment has been the subject of numerous and exhaustive investigations[3].

In spite of the extensive information available, the mechanism of the formation of bound-rubber has not yet been satisfactorily explained. This paper gives the results of an electron-microscopic investigation of the system: filler-bound rubber, which throws further light on the structure of the rubber-filler mixture.

Mixtures containing gas black CK3, the finely divided pyrogenically prepared silicic acid (Aerosil), and the calcium silicate filler, Calsil, have been studied. The proportions, in parts by weight, based on 100 parts of natural rubber, were as follow:

CK3 Black	Aerosil	Calsil
58	36	60

The mixtures were prepared on a laboratory roll mill at a mixing temperature of 50° C and time of eight minutes, and were passed nine times between closely set rolls.

The samples were prepared for extraction by the following procedure. By means of the Conti type of Defo apparatus for preparing samples, cylindrical samples 10 mm. in diameter were dried out from the mixtures, and these were divided into discs 0.5 mm. thick on a special holder. Two-gram samples were weighed for extraction in every case. The extraction was begun after a 24-hour steeping period of the samples at room temperature. They were then extracted with benzene in a Soxhlet apparatus for 7 × 24 hours. The bound-rubber component values in percentages of the filler were:

CK3 Black	Aerosil	Calsil
45	32	20

(By a comparison of the bound rubber contents, it is possible to evaluate the various grades of fillers.)

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by (Miss) Leora Straka from *Kautschuk und Gummi*, Vol. 5, No. 2, pages WT17-22, February 1952. This paper was presented at a meeting of the German Rubber Society at Bad Neuenahr, October 12, 1951.

In virtue of their transparency, the mixtures containing Aerosil permitted a few observations concerning the structure of the extraction residue. In Figure 1, *a* represents a sample prepared for extraction. The cross drawn on the supporting base is visible through the sample. The color of the sample is that of the processed rubber. The symbol *b* represents a disc of the same sample after extraction with benzene. It is completely opaque and is almost white. Under

FIG. 1.—Tests of batches loaded with Aerosil.
(a) Sample before extraction.
(b) Sample after extraction with benzene.
(c) Sample extracted with benzene and then strongly compressed.

the microscope a very fine grooving on the surface of the extracted sample can be seen, caused by the cutting operation in the preparation of the sample. The symbol *c* represents an extracted disc which was strongly compressed between smooth metal sheets after extraction. Thereby the sample again assumes its original color and is completely transparent, as is evident by the renewed visibility of the cross marked on the supporting base. From these observations it can be concluded that:

(1) In the case of the type of filler under consideration, the filler and bound-rubber form a stable structure, so that, by extraction, during which the major portion of the rubber is removed, the form of the test-specimen remains the same, even in its details.

(2) By removal of the soluble component of the rubber, a spongelike structure is formed, which, because of the many-phase boundary surfaces, is opaque and appears white.

(3) The hollow spaces in the extraction residue can be closed again by mechanical pressure, whereby the reflecting phase boundaries disappear, and the sample regains its color and transparency.

The purpose of the electron-microscopic investigation was to throw further light on the structure of the system: filler-bound rubber, and to prove definitely its foamlike structure. Furthermore, the purpose was to determine to what extent the rubber which has been chemically changed by the influence of the filler and thereby rendered insoluble in benzene, still resembles in its physical properties the unchanged rubber.

First of all, the behavior of natural rubber when spread while swollen in benzene is shown on a specimen screen in the electron microscope.

Smoked sheet was swollen for several hours in pure benzene and then carefully spread on a specimen screen, and was allowed to stand at room temperature in order to evaporate all of the benzene. The electron microscopic picture (Figure 2) shows a system of rubber bands and filaments of various widths and diameters. The geometry of these filaments shows that the stresses within the entire system are in complete equilibrium. The filaments are in some cases very thin and have in many cases a structure resembling a string of pearls, in which thinner and thicker sections alternate along the filament. After evaporation of the benzene, even the thinnest filaments can not be redissolved in

benzene. Obviously the entire filamentary substance has been oxidized by atmospheric oxygen, and its solubility thereby changed. The rapidity of this process is explained by the small diameter of the filaments.

Here it should be pointed out that electron micrographs of organic substances must be interpreted with particular care. The behavior of thin rubber films in the electron microscope is illustrated in Figures 3a and 3b. A thin

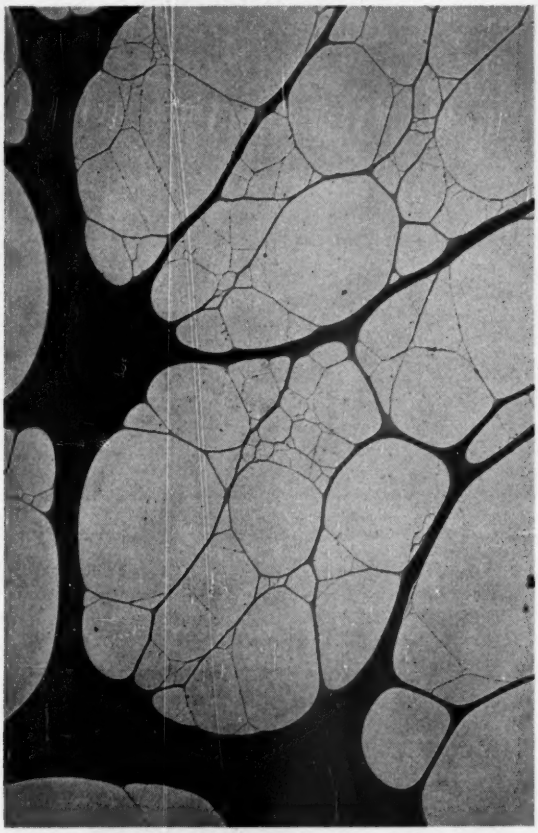
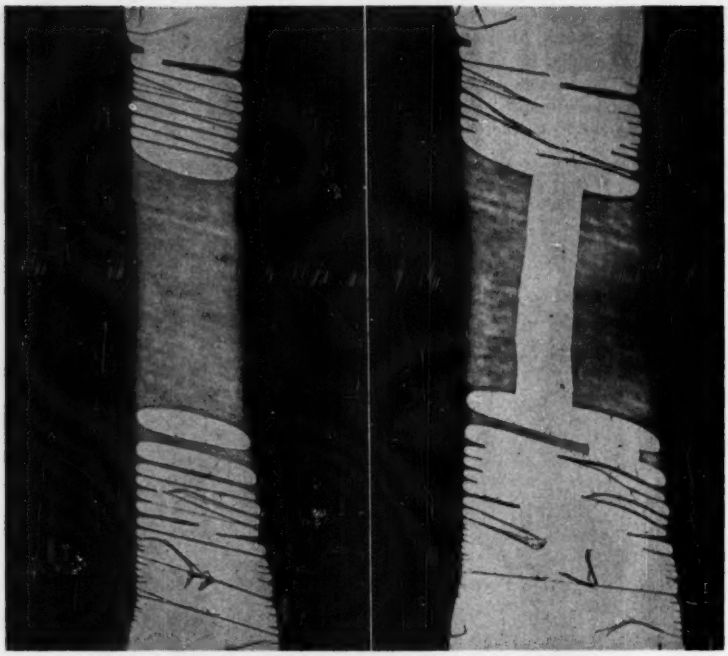


FIG. 2.—Natural rubber swollen in benzene and spread out. Magnification 10,000:1.

SiO film was vaporized on a collodion film, such as is usually used as a supporting film for the preparation of electron microscopic specimens in order to protect the collodion from attack by organic solvents. A drop of a dilute rubber solution was placed on the SiO layer, and the benzene used as the solvent was evaporated at room temperature. In this way a very thin firmly attached rubber film was obtained on the collodion film. Under the electron microscope and at one position of the specimen beyond the focused field of vision, the collodion film was ruptured by intensive exposure to electrons. The rupture ex-



a b

FIG. 3.—Natural rubber film torn under the electron microscope. Magnification 10,000:1.

tended outward from the damaged position over a rather large area of the specimen which had not been subjected to the intense exposure.

Figure 3a shows that the rubber membrane stretched over the collodion film at first behaves as would be expected. It forms thin filaments, which obviously are very easily deformed. In the middle of the picture a relatively

FIG. 4.—Microtome slice of an extracted batch of CK-3 rubber. Magnification 20,000:1.

broad web of the membrane shows a fine granulation. After a few minutes, rupture of the collodion film was extended by a corresponding stress at a position again outside of the photographic sector. As Figure 3b shows, the rubber between these ruptures is degraded and probably is converted into a finely crystalline carbon. It now has hardly any plastic-elastic properties, but ruptures like a glass film with smoothly broken edges.

FIG. 5.—CK-3 bound rubber, wet with benzene and spread out. Magnification 20,000:1.

In order to get a general view of the magnitude of the hollow spaces in the extraction residues, the extracted sample of a mixture loaded with black (CK-3) was embedded in Celloidin and cut at the temperature of liquid carbon dioxide on a sliding microtome. The material cut badly, and there was a very strong tendency to tear.

Figure 4 reproduces the peripheral portion of such a rupture at a magnification of 20,000. The foamlike structure of the extraction residue can be recog-

nized. The size of the individual hollow spaces is approximately the same magnitude as the dimensions of the filler particles. The rubber portion, i.e., the bound rubber, which did not dissolve during the benzene extraction is present in part as a connecting adhesive between the filler particles.

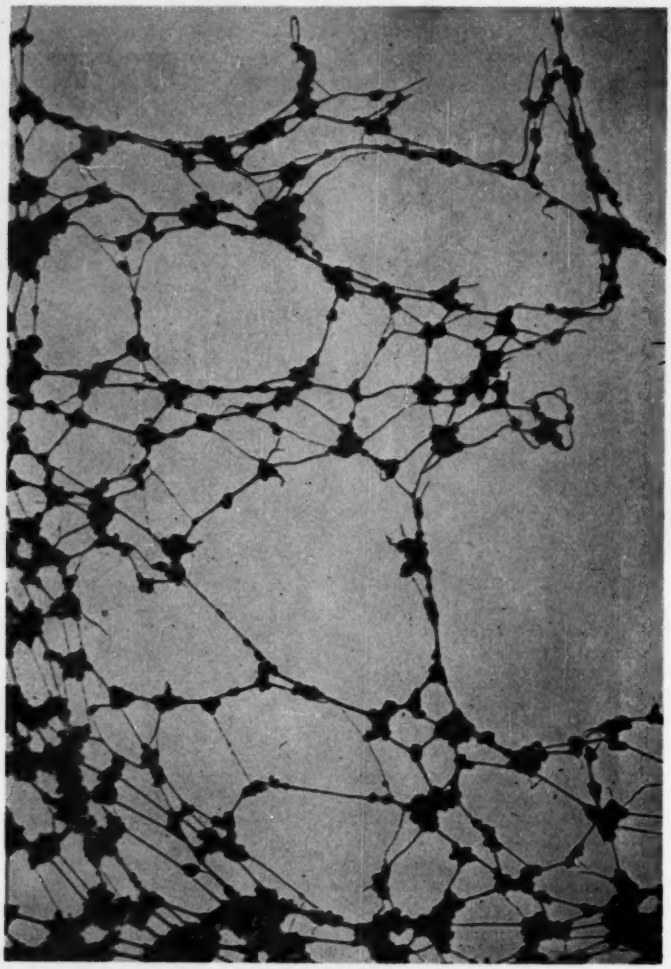


FIG. 6.—CK-3 bound rubber, wet with benzene and spread out. Magnification 20,000:1.

The preparation of further specimens for electron-microscopic examination of the bound-rubber extraction residues was carried out in a manner similar to that which has been described for the preparation of the swollen natural rubber. A sample of the extraction material, still moist with benzene, was carefully

placed on a specimen screen and slowly transferred from it. In this case the motion was in the plane of the supporting film.

The left half of Figure 5 illustrates a portion of the still almost completely coherent structure of the extraction residue. The system: filler/bound rubber, has been developed as a result of mechanical stress during the spreading operation. This structure consists primarily of broad bands in which individual

FIG. 7.—Aerosil-bound rubber. Magnification 20,000:1.

particles of carbon black are visible (lower part of the illustration). These bands have been spread to form thin filaments which connect larger islands of filler aggregates with one another, and here and there individual filler particles adhere to them or are embedded in them.

Figure 6 shows a section of the same preparation shown in Figure 5, which has been very greatly stretched and in which practically nothing but very thin filaments with individual islands of filler are present.

Similar pictures were taken in the electron microscopic investigation of extraction residues of mixtures containing Aerosil. Figure 7 shows that the system of Aerosil and bound rubber, which at first is completely coherent, spreads apart when subjected to a mechanical force and forms the system of filaments and filler-islands with bound rubber adhering to them. Figure 8 shows a section which is under greater mechanical stress.

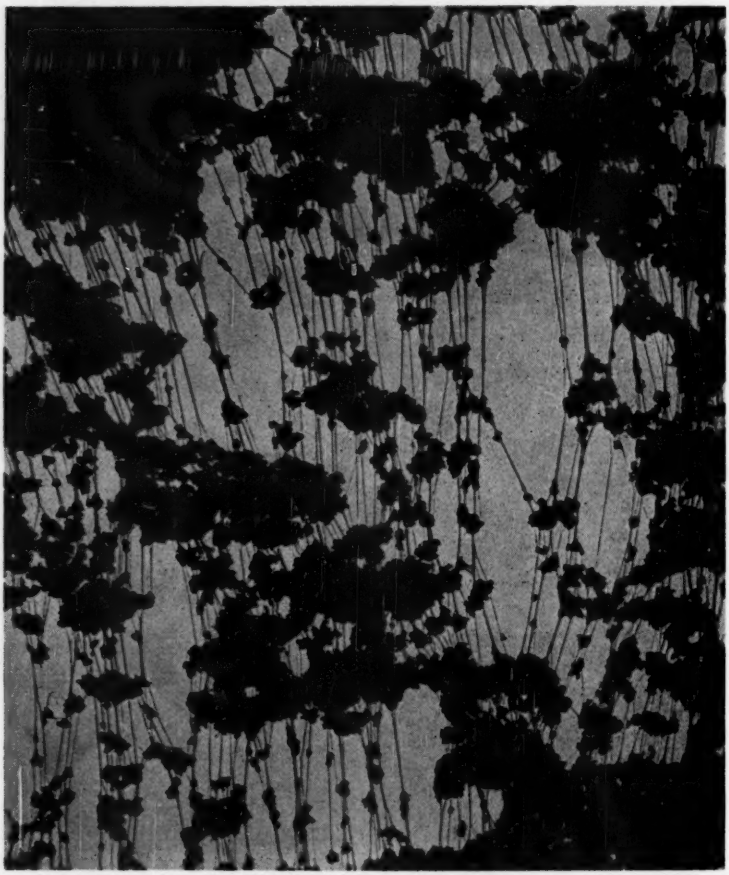


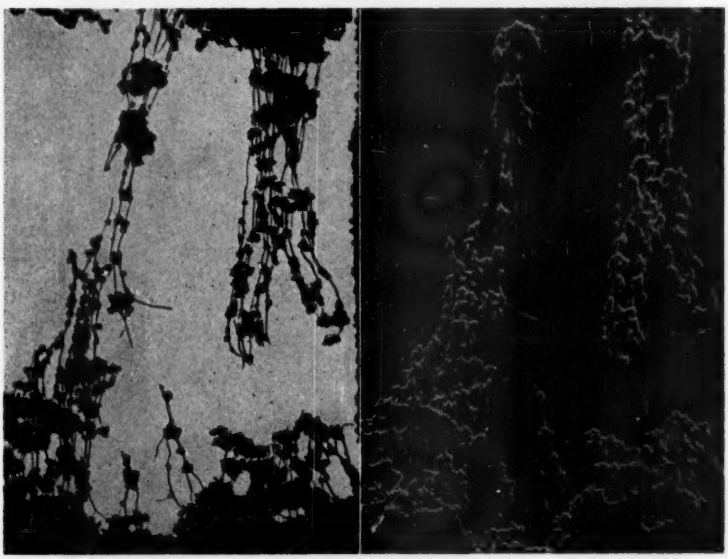
FIG. 8.—Aerosil-bound rubber. Magnification 20,000:1.

Figures 9a and 9b show the same preparation, first in a light field and then in a dark field. The dark-field picture impression gives a three-dimensional or stereoscopic effect.

Figure 10 shows the extraction residue prepared from a Calsil mixture. In spite of this relatively high grade filler, this residue contains only about two-thirds of the bound rubber of the Aerosil mixture. This is evident in the

photograph by a loose structure and by a relatively slight tendency toward filament formation. Individual large clots are formed, and these tear apart very easily where they join. Here the rather small portion of plastic component has a very definite effect. The photograph of the extraction residue shows that the mechanical properties of the bound rubber have not changed in any essential way, but that the bound rubber behaves, under comparable conditions, very much like the unchanged natural rubber. The ability to form very thin filaments in the benzene-swollen state definitely characterizes both materials as the same.

Filament formation in the bound-rubber preparations indicates that the bound rubber is not firmly attached to the surfaces of the filler particles, but is



a b

FIG. 9.—Aerosil-bound rubber, taken in a bright field and in a dark field.

able to flow from there to the structure of the filaments through rather large distances.

Therefore in a first approximation, the mixtures of rubber and filler are to be regarded as a three-phase system in which the filler particles, the bound rubber component, and the unchanged natural rubber are present as three coexisting phases. By extraction with benzene, the unchanged natural rubber is removed from this system. In the extraction residue, empty spaces are present at the positions where the soluble natural rubber is located, while the bound rubber portion remains between the filler particles, surrounds them, and binds them to one another.

This description is very similar to the concept of Sweitzer and his coworkers[3] with respect to the structure of the filler-rubber mixture, and according to which a type of three-dimensional "lattice,," is formed in which filler/bound rubber

units are joined to one another by unchanged rubber. The Sweitzer view, however, differs in that the primary "lattice" unit is constructed of filler particles which are surrounded by bound rubber and connected to one another, while the unchanged rubber fills the interstices of this lattice.

The amount of bound rubber which is formed by the individual fillers in the mixture, and the strength of the resulting structure, must affect the plastic-elastic properties of the mixture. Indicative of this fact is the behavior on deformation, which was judged in an approximate way with the Defometer, by

FIG. 10.—Calsil-bound rubber. Magnification 20,000:1.

the method of Baader. Mixtures with high contents of bound rubber show high Defo hardness values, *i.e.*, a comparatively great force is necessary to deform them. Conversely, it is possible to make an approximate estimate from the Defo values of the amount of bound rubber formed in the mixture.

No direct conclusion can be drawn from the results with the electron microscope about the chemical structure of the bound rubber itself and the nature of its formation. Furthermore, the assumption of an adsorptive bond of the rubber through surface forces of the filler particles does not seem sufficient to explain the behavior of the bound rubber-filler system as it appears in the electron microscope. It is much more probable that, under the influence of the

electrostatic surface forces of the filler particles, cross-linking of the rubber molecules with one another is brought about by C—C bonds. The larger molecular units which result are no longer soluble in benzene. The nature and the extent of the cross-linking can be determined by the number and intensity of the active interference patterns which are present on the filler surfaces in the sense described. The details of this idea will be described in a later paper.

SUMMARY

Electron microscopic investigations of the benzene-extraction residues of filler-natural rubber mixtures which are used for the determination of bound rubber, give a pattern of a three-dimensional network consisting of filler and bound rubber. The unchanged benzene-soluble rubber is present in the interstices of the network in the untreated filler-rubber mixture.

ACKNOWLEDGMENTS

A part of the very difficult preparatory work was carried out by E. Schüller. The electron microscope pictures were taken by H. Gebauer. The instrument used was the Zeiss electrostatic microscope, Type EM 7.

REFERENCES

[1] Le Blanc, Kröger, and Klos, *Kolloidchem. Bei.* **20**, 356 (1925).
[2] Fielding, *Ind. Eng. Chem.* **29**, 880 (1937).
[3] Sweitzer, Goodrich, and Burgess, *Rubber Age* (N. Y.) **65**, 651 (1949).

VITRIFICATION OF HIGH POLYMERS IN PERIODIC DEFORMATION *

G. M. BARTENEV

SCIENTIFIC RESEARCH INSTITUTE OF THE RUBBER INDUSTRY, MINISTRY OF THE CHEMICAL INDUSTRY, MOSCOW, USSR

As is known, high polymers are readily supercooled and retain their amorphous structure below their crystallization points. Changes of the physical properties in the temperature range of crystallization are a linear function of temperature. When the temperature is lowered further, high polymers remain in their amorphous liquid state; this is indicated in particular by their retaining their high elastic properties below the crystallization temperature. However, with further decrease of temperature, the linear character of the changes of physical properties is no longer evident, and the latter undergo more or less abrupt anomalous changes. In particular, there is a change of the polymer from the amorphous-liquid state with high elasticity into a hard vitreous form, which, as is known, is not related to changes of the structure of high polymeric substances. Vitrified polymers, like amorphous liquids, possess amorphous structures. A number of investigators[1] have found similar anomalies in the heat capacity, heat expansion, dielectric properties, and high elastic properties of various polymers during transition to the vitreous state.

The temperature of the change from an amorphous liquid to the vitreous state will be indicated by T_g. However, at present there is no generally accepted definition of what is understood by the temperature T_g. Tammann[2], for example, regards T_g as the conventional temperature of brittleness. This definition is unsuitable, because T_g depends on the method of determining the brittleness temperature. Kobeko[3] defines T_g as the lower limit of the softening range within which transition from the laws of the solid to those of the liquid state takes place. Alexandrov[4] and Kobeko[3] call T_g the temperature of vitrification, below which second-order equilibrium cannot be established. As a result, the structure in the vitreous state remains unchanged during lowering of the temperature, and the decrease of volume is due to the change of the average distance between the particles, as in solid substances.

Alexandrov[5] determined the numerical value of T_g by extrapolation of the tangent on the temperature axis to the point of inflection of the deformation-temperature curve.

Kargin and Slonimskiĭ[6] related T_g to the dynamic behavior, increase of active forces, and sensitivity of the apparatus for measuring deformation, and regard T_g as the conventional temperature.

The investigations of Kobeko, Alexandrov, and others[7] have established that vitrification of polymers takes place gradually and not abruptly in a certain temperature range, and that transition to the vitreous state is not a phase process, but is caused by the high relaxation nature of high-elastic de-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Doklady Akademii Nauk Soyuza Sovetskikh Sotsialisticheskikh Respublik*, Vol. 69, No. 3, pages 373–376 (1949).

formation. Consequently the region of vitrification, T_g, depends on the condition of deformation; for example, on the deformation frequency.

Kobeko, Tammann, and others also observed that transition to the vitreous state depends on the different physical properties of the amorphous liquid state.

The process of transition to the vitreous state will henceforth be called simply vitrification, just as transition to the crystalline state is called crystallization. Although these processes are quite different physically, they are similar to the extent that both take place principally in a definite temperature range. In the case of vitrification, the corresponding temperature interval will be called the region of vitrification, or Kobeko's range of softening in the case of passage from low to high temperatures.

Comparing vitrification with equilibrium crystallization, we see that the latter proceeds in a much shorter, but nevertheless in a quite definite temperature range[8]. The crystallization temperature T_s corresponds to the temperature

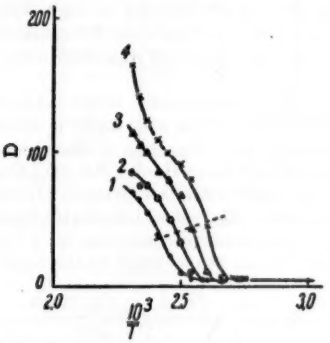


FIG. 1.—Curves of the amplitude D in conventional units as a function of the reciprocal temperature for polystyrene (the broken line crosses the inflection points).

1. Frequency of 1000 min.$^{-1}$
2. Frequency of 100 min.$^{-1}$
3. Frequency of 10 min.$^{-1}$
4. Frequency of 1 min.$^{-1}$

with a maximal heat effect of crystallization or to the point of inflection of the heat-content curve.

Vitrification takes place in a temperature interval of several degrees or more. The heat capacity, coefficient of thermal expansion, deformation, and other properties change with the temperature, and give curves with points of inflection (see Figure 1).

It is, therefore, quite reasonable to define T_g as the vitrification temperature, represented by the point of inflection of the curves. Tammann gave the point of inflection the designation T_w, identifying the process of vitrification with the transition point. In this connection we should note that analogous definitions of T_g were adopted at the International Congress on Glass[9]. The advantage of this definition is that the temperature T_g is no longer of an arbitrary nature. For a given physical property, it depends only on the experimental conditions, and is a specific property of high-elastic materials which depends on their relaxation characteristics. At the points of inflection on these curves, the physical properties change more abruptly.

The conventional temperature of vitrification as understood by Kobeko and Alexandrov can be appropriately designated by another term, for example, T'_g. According to Tammann, this temperature T'_g coincides with the brittle temperature T_b; according to Kargin and Slonimskiĭ, it depends also on the sensitivity of the measuring apparatus.

Kauzmann[10] defines T_g as the temperature at which the heat capacity and coefficient of expansion of a liquid show the greatest changes, provided that the time necessary to establish equilibrium for measurements fall between 10 and 60 minutes. This definition is unsatisfactory because it selects only two of the many physical properties for defining T_g, which give almost the same values for T_g, and, besides, relates T_g to arbitrarily chosen experimental conditions, which is inadmissible. Since T_g depends on the physical property studied and on the experimental conditions, the problem becomes one of an investigation of the dependence of T_g, for various physical properties of the given material, on the experimental conditions, and a comparison of the results obtained.

Let us examine the case of vitrification of high polymers during periodic deformations. The basic work, in which the influence of the frequency of deformation on the vitrification of a polymer was determined is that of Alexandrov and Lazurkin[11].

In interpreting the experimental data, these authors proceeded from the assumption that the total deformation with uniform stress is the sum of elastic and high-elastic components: $D = D_{\text{elasticity}} + D_{\text{high elasticity}}$. Here the elastic component of the deformation follows Hook's law, and the high-elastic component follows the law of an elastic-viscous substance (Kelvin's modulus). If E_0 represents the elastic modulus, E_∞ is the high-elastic modulus, and if we bear in mind that $E_0 \gg E_\infty$, then Alexandrov's modulus for a highly elastic substance which undergoes periodic deformations leads to the following equation:

$$D = \frac{\sigma_0}{E_\infty}\sqrt{\frac{1 + (E_\infty/E_0)^2\omega^2\tau^2}{1 + \omega^2\tau^2}} \tag{1}$$

where D is the deformation, σ_0 is the stress, ω is the frequency of deformation, and τ is the mean time of relaxation.

The experiments showed that, when σ_0 is constant, the D-T curve has a point of inflection, and is displaced by a change of the deformation frequency.

Using the well known formula for the relaxation time:

$$\tau = \tau_0 e^{U/(kT)} \tag{2}$$

we have:

$$\ln \tau = \ln \tau_0 + \frac{U}{kT} \tag{3}$$

Accepting the deformation in Equation (1) as a function of $\ln \tau$, we find that the inflection on the $D = f(\ln \tau)$ curve corresponds to the following:

$$\omega\tau = \text{const.} = \sqrt{2} \tag{4}$$

From this we obtain an equation relating T_g to the frequency:

$$\ln \omega + \frac{U}{kT_g} = \ln \sqrt{2} - \ln \tau_0 \tag{5}$$

The energy of activation U is itself a function of the temperature. However, as Alexandrov and Lazurkin showed, for many polymers, the relation between

ln τ and $1/T$ is nearly linear. Consequently, U is only an approximate function of the temperature within the temperature range studied. Therefore, without danger of significant error, instead of the $D = f(\ln \tau)$ curve for the measurement of the temperature T_g by the point of inflection of the curve in the coordinates, D and $1/T$, can be used as coordinates of a curve.

The curves of polystyrene at different frequencies, calculated from Malinski's data, are given as examples in Figure 1.

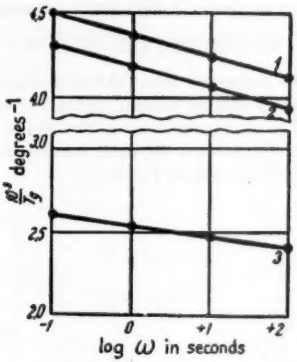


FIG. 2.—Relation of the reciprocal temperature of vitrification to the logarithm of radial frequency.

1. Natural rubber
2. Polychloroprene
3. Polystyrene

Figure 2 gives data on the vitrification temperature as an inverse function of the logarithm of the radial frequency: $\omega = 2\pi\nu$, for various polymers. The linear relations in Figure 2 confirm experimentally Equations (4) and (5).

REFERENCES

[1] Bekkedahl, *J. Res. Natl. Bur. Standards* **13**, 411 (1934); Bekkedahl and Matheson, *J. Res. Natl. Bur. Standards* **15**, 503 (1935); Tammann, "The Vitreous State" State Sci.-Tech. Press. **1935**; Kobeko, Kuvshinskii, and Gurevich, *Doklady Akad. Nauk SSSR* (Phys. Ser.) **3**, 329 (1937); Alexandrov and Lazurkin, *Kautchuk i Rezina*, No. 10, 34 (1939).
[2] Tammann, "The Vitreous State", State Sci.-Tech. Press, 1935.
[3] Kobeko, "The Amorphous State", GTTI, 1933; Kobeko, "Physical-Chemical Properties of Dielectrics", State Chemical Press, **1934**, pp. 185, 192, 195.
[4] Alexandrov, "Reports of the 1st and 2nd Conferences on High Molecular Compounds", Acad. Sci. USSR., **1945**, p. 49.
[5] Alexandrov and Lazurkin, *Doklady Akad. Nauk SSSR*, **43**, 396 (1944).
[6] Kargin and Slonimskii, *J. Phys. Chem.* **23**, 568 (1949).
[7] Kobeko, Kuvshinskii, and Gurevich, *Doklady Akad. Nauk SSSR* (Phys. Ser.) **3**, 329 (1937); Alexandrov and Lazurkin, *Kautchuk i Rezina*, No. 10, 34 (1939); *Doklady Akad. Nauk SSSR*, **43**, 396 (1944).
[8] Bartenev, *J. Phys. Chem.* **22**, 587 (1948).
[9] *J. Soc. Glass Technol.* **14**, 159 (1930).
[10] Kauzmann, *Chem. Revs.* **43**, 219 (1948).
[11] Alexandrov and Lazurkin, *Kauchuk i Rezina*, No. 10, 34 (1939).

PLASTICITY AND FILLER STRUCTURE IN CARBON BLACK STOCKS *

R. W. WHORLOW

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

EXPERIMENTAL RESULTS

An earlier investigation[1] showed that rubber stocks containing fillers possess an internal structure which can be broken down by working and which forms again on standing. This structure makes the stock stiffer. The extent of structure formation and breakdown depends on the nature of the filler, and is most evident with reinforcing carbon blacks.

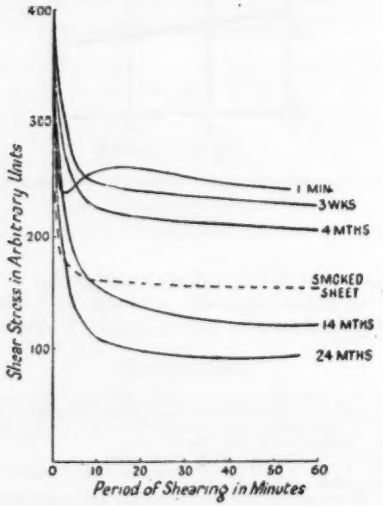


FIG. 1.—Influence of long-period room temperature storage on the properties of a carbon-black masterbatch.

The study of structure formation in carbon black stocks during storage has now been extended to much longer storage periods. The changes were examined by tests in the shearing-cone plastometer[2], the tests being sufficiently prolonged to show the structure breakdown produced by continuously shearing the stock.

Figure 1 shows a plot of shear stress (in arbitrary units) against period of shearing for a 100/50 smoked sheet/MPC black masterbatch sheared at 1 radian per second after 1 minute preheating at 100° C in the shearing-cone plastometer. These curves were determined after various periods of storage

* Reprinted from the *India-Rubber Journal*, Vol. 125, No. 7, pages 252–254, August 15, 1953. The present address of the author is the Battersea Polytechnic, London, England.

of the stock at room temperature. The first three curves were given in the earlier paper[1], to which reference should be made for further experimental details, but the curves for 14 and 24 months' storage have now been added, together with the curve (broken) for a smoked sheet sample masticated for the same period as the masterbatch.

These tests show that the initial stiffness of the stock increases with storage, but that this increased stiffness is lost very rapidly when shearing is commenced, as reported previously. The present results are interesting because of the very low level of stiffness reached after 24 months' storage, this being even lower than for the comparable smoked sheet sample, which did not change in properties with storage.

These results have been confirmed and extended by tests on a fresh sample of the same composition but rather softer. Figure 2 shows, on the left, a series

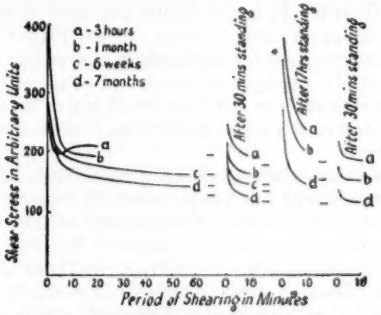


FIG. 2.—Detailed behavior of a carbon-black masterbatch after various periods of room temperature storage (3 hours to 7 months).

of curves similar to those in Figure 1, but for the new sample. After each of these curves was obtained, the sample was sheared for 10 minutes at 10 radians per second, and then for 10 minutes at 1 radian per second. The stress level at the end of this shearing is indicated next in Figure 2. The samples were then stored for 30 minutes at 100° C in the instrument and then sheared at 1 radian per second for 10 minutes giving the second set of curves in Figure 2. The sequence of shearing at 10 radians per second, 1 radian per second, storage and shearing at 1 radian per second, was then repeated twice, the second storage period being 17 hours, and the third again 30 minutes. The data (all refer to shearing at 1 radian per second) are given in graphical form on the right in Figure 2. The behavior is of the type discussed in detail in the earlier paper[1]. After the second shearing at 10 radians per second, the 1 radian per second stress has reached a value which can be reproduced after any subsequent treatment by a period of shearing at 10 radians per second. On standing, the rubber stiffens to an extent dependent on the period of standing, but the degree of stiffening in a given period (*e.g.*, 30 minutes) is less after prolonged storage at 100° C. Two new features are shown in these results. First, the differences in stress (after the first 20 minutes shearing) between the samples stored at room temperature for various periods are substantially maintained in all subsequent shearing, there being no apparent tendency for the samples to approach a common level of stiffness. Second, the increase of stress brought about by standing at elevated temperatures is roughly proportional to the stress required for shearing immediately prior to the standing.

DISCUSSION

An extension of the previous hypothesis[1] seems necessary to explain the observed behavior. The explanation given below, it is believed, explains all the major experimental features. The terms "structure" and "bonds" are here used rather loosely to include the effects of carbon-carbon or carbon-rubber interactions, as the results in themselves cannot differentiate between these mechanisms.

We assume that the masterbatch, immediately after mixing, contains a permanent structure ("permanent" in a sense discussed below), and also a number of "active centers," some of which form temporary "bonds" which stiffen the rubber, as does the permanent structure. When the rubber is allowed to stand, particularly at elevated temperatures, many more of these bonds form, while, during shearing, a dynamic equilibrium is set up between formation and breakdown of these bonds, as previously discussed in detail[1]. The samples tested soon after milling (Figure 1, 1-min. curve; Figure 2, curve *a*) contain fewer bonds than are required for equilibrium at 1 radian per second, causing the rising portion of the appropriate curves. Prolonged storage of the stock at 100° C causes a reduction in the number of active centers, with the result that less stiffening occurs in a subsequent given period of standing at this temperature (Figure 2).

It has been noted that, after considerable shearing at 10 radians per second, the stress required to shear at 1 radian per second is brought to a level which can be reached again after any subsequent treatment of the rubber not involving shearing at a rate above 10 radians per second. It is believed that the difference between this reproducible level of stiffness and that of the uncompounded rubber, that is, the stiffening effect of the carbon black, is due almost entirely to "permanent" structure, only perhaps 10 or 20 points (using the arbitrary scale on the graphs) being due to dynamic equilibrium effect involving temporary bonds. The reasons for this view are (1) the increase of stiffness during the first few minutes in the initial curves (Figure 1, 1-min. curve; Figure 2, curve *a*) is of this order; (2) the rise on shearing at 1 radian per second after shearing at 10 radians per second[1] is only a few divisions; and (3) although prolonged storage at 100° C reduces the ability of the stock to form structure by nearly 50 per cent, the reference level reached after prolonged shearing is altered only slightly if at all.

If this is the case, then the results of tests after very prolonged room temperature storage cannot be explained by assuming that most of the stiffening due to black is of a "dynamic" nature and that the only effect of long period storage is to reduce the number of active centers, thus reducing the reference level. It therefore appears necessary to assume that many of the bonds which are permanent for tests lasting up to 67 hours at 100° C in the shearing-cone plastometer, are broken or weakened during very long periods at room temperature. The only obvious agency present in the second case, but not in the first, is air, and since any agency present in both cases would be expected to have a considerably accelerated effect at 100° C, it seems necessary to assume some component of air, presumably oxygen, to be responsible for the long-period softening effects shown in Figure 1. If this is so, it strongly suggests that the bonds forming the permanent structure are chemical in nature. There remains the necessity to explain the effects of room temperature storage on tests in the Williams plastometer. It has been shown[3] that such storage causes some increase of stiffness, but also prevents any further stiffening on heating the

samples. Presumably some active centers form bonds, but the remainder become deactivated, so they have no effect when the samples are heated. However, as was shown above, long-period storage has little effect on the ability of the stock to form structure at 100° C after considerable shearing, presumably because this shearing breaks the temporary bonds formed during storage.

In the initial curves in Figures 1 and 2, the high stress when shearing is first commenced can be attributed partly to nonuniformity of temperature, and partly to some orientation effect of the rubber molecules alone. The subsequent slow rise, completed in about 15 minutes, is the approach to dynamic equilibrium by the active centers, while the eventual slow fall in stress to the reference level may be due to some breakdown of permanent structure by traces of oxygen (although the fact that the reference level of stress is independent of the period at 100° C argues against this), or to breakdown of some bonds of intermediate strength.

STRUCTURE IN VULCANIZATES

In view of the changes which occur during long room-temperature storage of a black masterbatch, it was of interest to determine the effect of such storage prior to vulcanization on a channel-black vulcanizate. A mix was prepared and sheeted out to a suitable thickness for molding test-sheets and stored. Sheets were vulcanized at intervals between 3 hours and 6 months after mixing without any remilling of the samples, and tested one day after vulcanization for (1) modulus before and after prestressing to break (using the double dumb-bell technique of Mullins and Newton[4]) and (2) tensile strength. No significant trend in any of the results was apparent, but, owing to the long period over which these tests occurred, the scatter of results was rather large. Further investigation will be necessary to show whether some component of the mix—for example, pine tar, used as a softener—influences the structure effects discussed above before any definite conclusions can be drawn from these results.

CONCULSIONS

The assumptions made above appear to account for the features of the behavior of MPC carbon-black masterbatches so far observed. However, there is scope for considerably more work on the properties of vulcanizates before a complete picture of the effects of channel black on the stiffness of rubbers is obtained.

SUMMARY

Continuing previous studies on the changes in stiffness of a carbon black masterbatch when stored at normal or elevated temperatures or when subjected to shear deformation, the changes during room temperature storage have been studied in more detail. From the results obtained, a modified hypothesis as to the behavior of carbon black structures in unvulcanized rubber is put forward, which accounts for all the features of the behavior of rubber/black stocks so far observed in this work.

REFERENCES

[1] Mullins and Whorlow, *Trans. Inst. Rubber Ind.* **27**, 55 (1951).
[2] Piper and Scott, *J. Sci. Instruments* **22**, 206 (1945).
[3] Whorlow, R. W., unpublished experiments.
[4] Newton, *Proc. 2nd Rubber Technol. Conf. London*, **1948**, pp. 241, 243.

RHEOLOGY OF UNMASTICATED AND MASTICATED SMOKED SHEET *

R. W. WHORLOW

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

1. INTRODUCTION

Present knowledge of the plastic properties of unvulcanized natural rubbers is of two types. First there are the results of tests on apparatus specifically designed to deform the rubber under closely defined conditions as to shear rate. The results of Mooney[1] and Hamm[2] on concentric cylinder instruments, and of Saunders and Treloar[3] on the shearing cone plastometer of Piper and Scott[4] have shown that, for masticated rubbers, the logarithmic plot of shear stress against rate of shear strain is slightly convex to the log stress axis, when determined under substantially equilibrium conditions at each rate of strain. Saunders and Treloar have studied one sample of mill-masticated smoked sheet in considerable detail, studying the temperature dependence of the relationship between stress and strain rate, while Mooney and Hamm have considered more than one type of rubber but not in detail.

The second type of information on the properties of these rubbers is that derived from observations with compression instruments, particularly that of Williams[5]. The most comprehensive study is that of Piper and Scott[6], who examined rubbers masticated or otherwise softened in various ways, and analyzed the results by the method of Scott[7]. The conditions of deformation in compression instruments are not well defined, a very wide range of strain rates being encountered, and although, as Scott has shown, it is possible to derive a value of n from the results if the Ostwald-de Waele law for deformation (strain rate proportional to the nth power of the stress) is assumed, the method cannot be considered satisfactory. However, Piper and Scott showed that the properties of a rubber vary widely with the method of softening used, although their results were not all obtained on samples derived from one batch of raw rubber.

The work described in this report was undertaken to extend that of the workers mentioned above by giving as complete a picture as possible of the behavior of the rubbers during deformation at elevated temperatures. Owing to the wide scope of the investigation, certain aspects only have so far been studied in detail, but it is believed that the results reported will clarify some important points, particularly:

(*a*) the extent to which the properties of masticated natural rubbers depend on the properties of the original rubber and on the method of mastication or plasticization;
(*b*) the amount of information necessary to define with reasonable precision the rheological properties of a rubber;
(*c*) the extent to which different test methods may, or may not, be expected to correlate with each other.

* This paper is a reprint of Research Report No. 68, March 1952, of the Research Association of British Rubber Manufacturers.

In addition, certain of the observations reported can be explained by the theory of mastication recently proposed by Pike and Watson[8], and may provide further evidence supporting their theory.

2. EXPERIMENTAL METHODS

Most of the results were obtained on the shearing cone plastometer of Piper and Scott[4]. This modified form of the Mooney viscometer[9] is designed to give a substantially uniform rate of shear strain throughout the rubber, and can be driven at any one of a wide range of strain rates. The advantage of this instrument is that it gives accurate relative values for the stiffness of different rubbers, and reasonably accurate absolute values, while being relatively easy to fill, clean, and operate. For the accurate determination of absolute values of stress and strain rate a concentric cylinder apparatus, with its attendant difficulties, would be necessary, but for the present purpose the shearing cone instrument is preferable. The strain rates and stresses quoted are probably only approximate as regards their absolute values.

For the softer rubbers the normal rotor of 1-inch radius, similar to that described by Piper and Scott, was used, but for stiff rubbers a rotor and die cavity scaled down in the ratio 1.44:1 in all dimensions was used to give a torque one-third of that for the normal rotor. It was found experimentally that the rotors did not give exactly equivalent results for shear stress, owing apparently to certain small differences in the construction, particularly the size of the grooves used to grip the rubber. Results in Figures 1 to 5 were obtained with the normal rotor, and those in Figures 6 and 7 with the small rotor; the two sets of figures should not be compared quantitatively.

With the stiffer rubbers at the highest strain rate (10 radians per second) a considerable temperature rise is to be anticipated in the rubber[10]; for a given rubber this would be only half as great for the small rotor, but all the recorded stress values at the highest strain rate should be regarded as low, the softening due to temperature rise being greater the stiffer the sample.

Some tests were made on the Williams plastometer[5] at 100° C, using 1-cc. cylinders compressed (after 15 minutes' preheating) by a 5-kg. load. Two types of test were made. In the first, test-pieces were compressed for 30 minutes, the thickness in the compressed state being noted at frequent intervals; these results were used to determine n values by the method of Scott[7]. In the second, compression was for 3 minutes, and the test-pieces were then allowed to recover for 3 minutes at the test temperature, allowed to cool for 15 minutes, and then measured for recovered thickness. This was done merely to give some indication of the elastic properties of the rubber; other methods such as have been discussed elsewhere[11], in which the rubber recovers after uniform shearing, would be preferable.

All mill mastication was carried out on an 18 × 8 inch laboratory mill with friction ratio 1.5:1 and a front roll speed of 30 ft. per min. For hot milling the rolls were kept as nearly as possible at 52° C; for cold milling the rolls were water cooled. During hot milling the rubber formed a band on the front roll in the usual way. For cold milling a different procedure, intended to keep the rubber as cool as possible, was used; the rubber was passed through the nip and then allowed to cool for 15 seconds before being folded in half and again passed through the nip, this procedure being repeated as often as was necessary to soften the rubber adequately.

The internal mixer was a size B Banbury with steam passing through the rotors for hot mastication, and with water circulating through rotors and casing for cold mastication.

3. PROPERTIES OF MASTICATED SMOKED SHEET

3.1 Typical behavior

The general behavior found for masticated rubbers will be illustrated by tests on a sample hot-milled for 20 minutes, and is typical of all the masticated samples.

3.1.1 Effect of period of shearing

Consider a sample preheated for 1 minute in the shearing-cone plastometer at 100° C, and then sheared at 1 radian per second. The stress required rises to

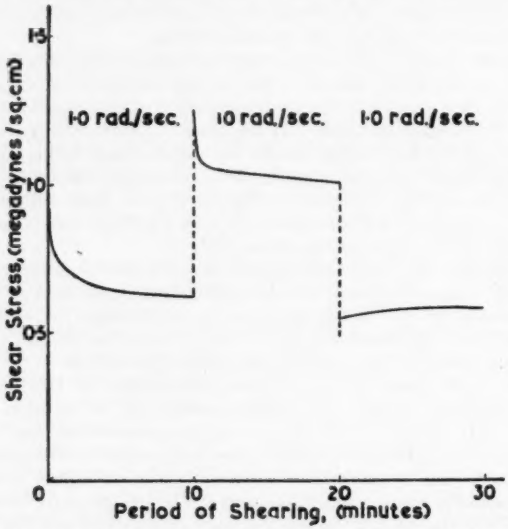


Fig. 1.—Variation of shear stress with period of shearing for masticated smoked sheet at 100° C.

a peak (Figure 1), then falls at first rapidly and finally very slowly for a long period. The shape of the initial part of this curve depends on a number of factors, such as the temperature of the rotor when inserted in the plastometer which make it variable for any one rubber, and, in consequence, only large differences in this part of the curve as between different rubbers are of any significance. If the sample is now sheared for a few minutes at 10 radians per second, a similar curve at a higher level of stress is obtained, while subsequent shearing at 1 radian per second yields a curve which rises slightly and then settles to a steady value below that reached before shearing at the higher rate. Subsequent shearing at any rate has little effect on the value reached after a short period at 1 radian per second.

For stiffer samples the behavior was qualitatively similar, except that longer shearing at 10 radians per second was necessary before a stable stress value was

reached. A "stable" value here means that the stress dropped by less than 3 per cent during the last 10 minutes shearing at 10 radians per second; once the rubber had reached this stable value, no important change occurred in its properties during subsequent tests. This behavior resembles qualitatively the behavior of carbon black masterbatches in the shearing-cone plastometer[12]. However, the changes in stiffness and the period of shearing necessary to achieve a stable shear stress at a given rate of strain are much less for rubber free from fillers. This incidentally makes the study of stiffness changes after various treatments of the rubber in the plastometer more difficult to follow accurately.

3.1.2. The stress/strain-rate curve

The next sequence of tests normally made was to shear the rubber in succession at 1.0, 0.1, 0.001, 0.1, 1.0, 10.0, finally 1.0 radians per second for about

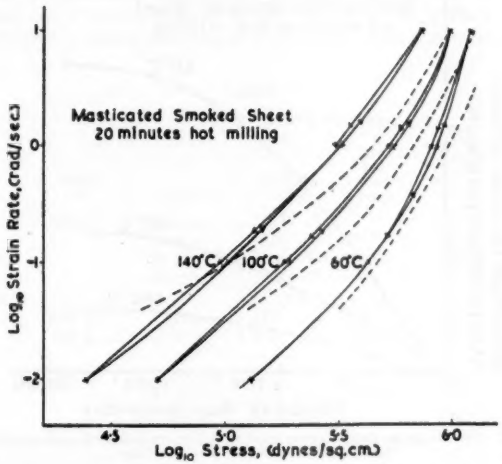


FIG. 2.—Logarithmic shear-stress/strain-rate curves for masticated smoked sheet at various temperatures. The dotted curves are from the paper by Saunders and Treloar.

5 minutes at each rate, a steady stress value being obtained in this time. Figure 2 (center curve, full line) shows the logarithmic stress/strain-rate plot for such a series on the sample hot-milled for 20 minutes (referred to above) tested at 100° C, the direction of change of strain rate being indicated by arrows. A slight hysteresis effect is apparent, stresses at a given rate being greater if the test is preceded by a low speed shearing than if preceded by high-speed shearing. This effect is, however, very small and may be ignored for most purposes. In many graphs given subsequently the center line of such a loop is taken as a unique stress/strain-rate curve for the sample. Some tests of this type have been carried out using a larger number of strain rates, giving smaller distances between experimental points, but since the increase of precision of the curves was only slight, it was considered preferable for most tests to economize in time by using only the four rates mentioned above.

The hysteresis loop is very narrow even for lightly masticated or unmasticated natural rubber, provided that sufficient shearing at the highest rate is given before the cycle of shearing at various rates is commenced. This appears to contrast with the behavior of GR-S, as reported by Piper and Scott[13] and by Treloar[14], for which hysteresis effects occur; moreover, GR-S requires much longer shearing to reach a constant stress reading, if indeed it ever does.

3.1.3. Effect of temperature

The behavior described above for masticated natural rubber tested at 100° C is found also at other temperatures. Figure 2 includes stress/strain-rate curves for the same sample at 60° C and 140°. These results are comparable with those of Saunders and Treloar[3], since, by chance, the rubbers are not greatly different in stiffness. The dotted curves in Figure 2 are taken from

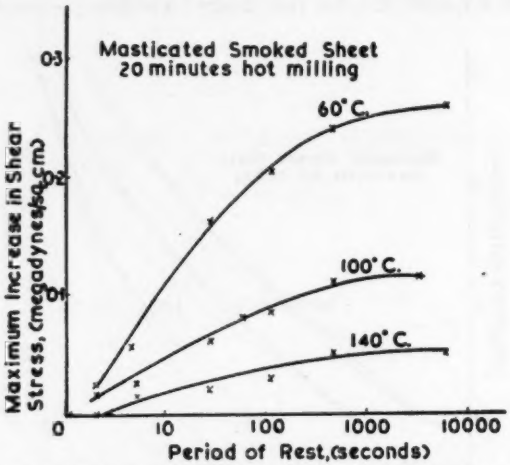


FIG. 3.—Maximum increase in stress required to shear masticated smoked sheet at various periods after previous shearing.

Saunders and Treloar's data at the corresponding temperatures. The agreement is not as satisfactory as might have been hoped, although if the results at very low stresses are disregarded as not very reliable, the general shape of curve and the temperature dependence of stress are reasonably consistent. It is not possible to say whether differences in instrument, samples, or procedure account for the discrepancies, but it will be shown later that changes in mastication procedure alone can produce differences of this magnitude, so there is no evidence of serious discrepancy between the two sets of results. The full curves in Figure 2 agree with Saunders and Treloar's results in that the vertical distance between curves for different temperatures is substantially independent of stress.

3.1.4. Stiffening during rest periods

Following the determination of the stress/strain-rate curve as described above, concluding with shearing at 1.0 radian per second, the shearing was

stopped for one of a number of periods, successively, and then recommenced at the same rate. The stress rose to a peak and almost immediately fell to the level reached before the pause. After a few minutes' shearing, a further pause of different length was given, and in this way the curves in Figure 3 were derived by plotting the difference between the peak stress and the steady value against the logarithm of the period of pause. These curves were obtained at the same three temperatures as in Figure 2. The semilogarithmic curves in Figure 3 rise steadily for about 10 minutes and then flatten. They appear to fall again slightly at very long periods, *e.g.*, 24 hours, but this has not been shown in Figure 3, since there is some possibility of chemical changes in the rubber during such prolonged heating. The cause of this stiffening is discussed in Section 5.1.

3.2 Influence of method of mastication: shearing-cone tests

In view of the general similarity of results at various temperatures, the results reported below were obtained at 100° C only. In general, the sequence described above, involving shearing at a high rate until a steady condition was

Table 1

Details of Mastication Procedures

Type of mastication	Batch size	Period	Abbreviation	Mean roll temperature	Final rubber temperature	Notes
Hot milling	800 g.*	5 min.	HM 5		60° C	Nip 0.12 inch
		10 min.	HM 10	51° C	58° C	
		20 min.	HM 20		60° C	
		40 min.	HM 40		58° C	
Internal mixer:						
Hot	400 g.	5 min.	HB 5	94° C	105° C	
Cold	400 g.	10 min.	CB 10	15° C	72° C	
Cold milling	300 g.*	50 passes	CM 50		34° C	Nip 0.10 inch
		150 passes	CM 150	16° C	—	
		300 passes	CM 300		24° C	

* 50-gram samples were cut off during milling at each of the times stated.

reached, testing at a range of rates, and then determining the effect of short pauses was adopted, although it was confirmed in representative cases that it was immaterial whether the effect of pauses was determined before or after the range of shear rates was used.

The following samples were all obtained from a batch of blended smoked sheet, prepared on a mill from sheets from one bale with a minimum of mastication. For this part of the investigation it was considered preferable to use a blended sample, to be certain that the starting material was the same in each case, rather than attempt some method of random sampling of the original untreated sheets. The results of tests starting with untreated smoked sheet are given later (Section 4.3). Table 1 gives the mastication details for the various samples.

The results of tests on these samples in the shearing-cone plastometer with the normal rotor at 100° C are shown in Figures 4 and 5, the former giving the logarithmic stress/strain-rate curves (the mean of the stress values for increas-

ing and decreasing rates of strain being taken where necessary), and the latter the peak increase in stress (at 1 radian per second) plotted against the length of the preceding pause.

3.2.1 Stress/strain-rate curves

The full curves in Figure 4, showing the influence of various periods of hot milling, form a family showing that the rubber becomes softer with increasing period of mastication, this softening being evident at all the rates of shear used in the tests. The dashed lines, for hot or cold Banbury mastication, fit into the same family of curves, and curves for other periods of Banbury mastication (not shown, for clarity, in Figure 4) show similar behavior. However, the dotted lines in Figure 4 for samples milled cold cross the previous family of curves and form a group of much steeper curves.

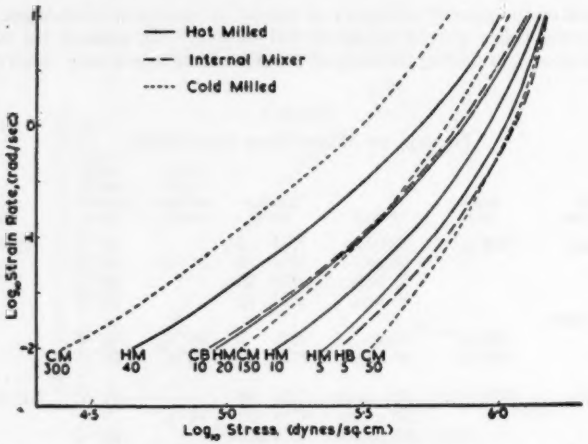


FIG. 4.—Logarithmic shear-stress/strain-rate curves at 100° C for smoked sheet masticated in various ways. (See Table 1 for key to curves.)

The obvious difference between the mastication conditions during cold milling and during the other types of mastication is the rubber temperature, since, although the rotors of the internal mixer were cooled for the CB experiments, the rubber was at a fairly high temperature. These results confirm the conclusion of Piper and Scott that a single parameter is inadequate to specify the properties of a masticated rubber in general, but show that a variety of fairly orthodox mastication treatments all give stress/strain-rate curves belonging to one family. The abnormally cold milling (CM) gives a different result, and judgment of the effects of some types of mastication used industrially, in which very high rubber temperatures occur, must be deferred until further experimental work has been carried out.

In general the curves in Figure 4 converge markedly at higher rates of strain, in the sense that the range of shear stresses required to strain different rubbers at a particular rate decreases with increasing stress. On the other hand, the vertical intercepts between curves of any one family are roughly independent

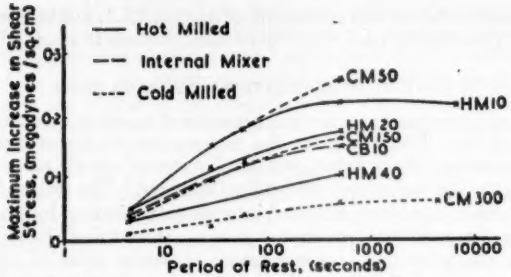


FIG. 5.—Maximum increase in stress required to shear masticated smoked sheet at various periods after previous shearing.

of shear stress, so that it cannot be concluded that differences in flow properties between different rubbers become less important at high shear rates. At the highest shear stresses, however, there are signs that the curves do converge vertically, in agreement with results for short milling periods (Section 4.2), but further data are needed to settle the point; in any case, the heating of the rubber caused by high strain rates could produce the observed convergence, so that it may prove to be a spurious effect.

A second series of similar tests was carried out on samples from a different batch of blended smoked sheet. The rate of softening for a particular method of mastication differed, but the stress/strain-rate curves for hot milling or for hot or cold mastication in an internal mixer fitted within experimental error into the family in Figure 4, and the cold milled samples again gave steeper curves. The corresponding curves to those in Figure 5 also fitted reasonably well.

Tests on the blended smoked sheet samples used as starting material for these two series, and on very lightly masticated samples, are considered in section 4.2.

3.2.2. Temporary stiffening

The results in Figure 5, showing the temporary stiffening when the rubber is allowed to rest, form a set into which all samples, including the cold-milled samples, fall in the same order as their stiffness at 1 radian per second from Figure 4, at least within experimental error. This means that no fresh information could be gained from such a measurement of temporary stiffening on a sample whose stress/strain-rate curve was known.

Cold-milled samples differed from the others in that the initial decrease in stress during the first plasticity measurement was much greater, as indicated in Table 2, which gives, for a selection of samples, the peak stress on commencing shearing at 1.0 radian per second (after 1 minute preheating at 100° C) and the final stress after conditioning at 10 radians per second and then shearing at 1.0 radian per second. The values should not be regarded as very reliable,

TABLE 2

PEAK AND FINAL STRESS VALUES AT 1.0 RADIAN PER SECOND FOR SAMPLES MASTICATED IN VARIOUS WAYS

Sample	HM 5	HM 10	HM 20	HM 40	CB 10	CM 50	CM 150
Peak stress (Megadynes per sq. cm.)	1.65	1.38	1.24	1.00	1.17	2.0	1.35
Final stress (Megadynes per sq. cm.)	1.05	0.91	0.74	0.53	0.70	1.13	0.64

for the reasons given in the first paragraph of Section 3.1.1, but indicate strongly that the more pronounced peak with cold-milled rubbers is a real effect.

3.3. Influence of method of mastication: Williams tests

Williams tests were made on the second series of masticated rubbers referred to in Section 3.2.1. Table 3 gives the compressed thickness after 3 or 30 minutes' compression, the n value, and the 3 minutes' elastic recovery for the untreated and the hot-milled and cold-milled samples. The results for hot and cold Banbury masticated samples fitted into the series formed by results on the hot-milled samples, and therefore are not given. In addition, Table 3 gives the shearing cone stress reading (normal rotor) at strain rates of 1.0 and 0.01 radian per second, and the mean slope of the logarithmic stress/strain-rate curve between rates of 0.1 and 0.01 radian per second. (If the Williams and shearing cone data were fully equivalent, this slope would approximately equal n.)

The hot-milled samples form a descending sequence of values for all tests, and so give a convenient scale of reference for comparing results on the other samples (the 5 minute sample was milled subsequently to the others, and the degree of breakdown was for some reason rather high, so that values for 5 and 10 minutes are unexpectedly close, but this does not affect the conclusions below).

3.4 Comparison of Williams and shearing cone results

The cold-milled sample (150 passes) at high strain rates appears softer than the 10 minute hot-milled sample, but at low rates it appears stiffer; this behavior is consistent with that discussed in Section 3.2.1. The 30 minutes' compressed thickness in the Williams test is consistent with the shearing-cone result at the lower strain rate, as might be anticipated from the low mean shear rate (0.01 radian per second or less) in the Williams test, but the 3 minutes' Williams value fits into the position in the sequence suggested by the 1.0 radian per second shearing cone tests. Thus, Williams compressed thickness/period of compression curves for the 10 minute hot-milled and 150 passes cold-milled samples cross in the same way as the corresponding shearing cone stress/strain-rate curves.

The next comparison is between the n values derived from Williams data, and the final column of Table 3, which is the slope of the logarithmic stress/

Table 3

Williams and Shearing-Cone Data for Masticated Smoked Sheet

	Williams data				Shearing-cone data		
	Compressed thickness (mm./100)		Recovery		Shear stress (megadynes/sq. cm.)		Mean slope
Sample	3 min.	30 min.	3 min. (mm./100)	n	1.0 rad/sec.	0.01 rad/sec.	0.1–0.01 rad/sec.
Blended smoked sheet	390	282	290	2.2	1.62	0.60	3.8
HM 5 min.	224	156	44	1.9	0.80	0.13	2.1
HM 10 min.	221	145	27	1.8	0.77	0.10	1.8
HM 20 min.	162	107	10	1.7	0.53	0.05	1.7
CM 50 passes	294	212	77	2.5	1.05	0.27	2.9
CM 150 passes	213	150	30	2.0	0.66	0.12	2.4

strain-rate curve at low rates. For a fairly soft rubber, obeying the Ostwald-de Waele law and showing no elastic effects, Scott's analysis[7] shows that these quantities should be equal, and Table 3 shows that there is agreement for the softest rubbers. For the relatively stiff blended smoked sheet much of the deformation in the Williams test is elastic, and no agreement between columns 5 and 8 would be expected. The results on the cold-milled sample (50 passes) show that the increase in n during this type of milling is not associated with a steepening of the shearing cone stress/strain-rate curve, and this may perhaps be associated with the elastic deformation superposed on the flow. Moreover, the slope of the logarithmic stress/strain-rate curve varies with strain rate, and the range of rates chosen for determining the slope in column 8 of Table 3 may not be appropriate for comparison with n values from Williams tests. In particular, the strain rates in Williams tests on stiff rubber will be less than for tests on soft rubbers, but it is doubtful whether the effect would be great enough materially to affect a comparison of columns 5 and 8.

The variation of n with degree of hot or cold milling is similar to that found by Piper and Scott[6].

The recovery results call for little comment, except that there is no great difference between the values for hot and cold masticated samples of the same plasticity. There is a suggestion that the recovery results correlate more closely with the 30 minutes' compressed thickness than with the 3 minutes' compressed thickness, but recovery tests are not sufficiently precise for much weight to be placed on this suggestion.

The data presented here are inadequate to justify any general conclusions, but they show that with the rubbers tested the agreement between results on the two plastometers is improved by considering low strain rate results for the shearing-cone instrument, and that there are probably no inconsistencies between results on the compression and rotation instruments which cannot be explained in terms of differences in strain rate. This conclusion was foreshadowed by earlier experiments[15], in which the agreement between Williams and Mooney tests was improved by using data for very short Williams compression times at which the strain rate is nearer to that in the Mooney test. The present results suggest that a knowledge of the complete stress/strain-rate curve for rubbers masticated in any of the ways considered may suffice to forecast the results to be expected from Williams compression or recovery tests. If this conclusion could be confirmed it would clarify the reasons for the anomalies frequently reported between results of Williams and Mooney tests, and would give valuable guidance on the extent to which a rapid compression type control test would be expected to give useful information.

4. UNMASTICATED SMOKED SHEET

The behavior of unmasticated smoked sheet is more complex than that of masticated rubber, and differs considerably from sample to sample. The behavior is described in Section 4.1 in some detail for what is believed to be a typical sample. Data on a wide range of samples are considered in Section 4.3, while Section 4.2 deals with the transition from the behavior described in Section 4.1 for unmasticated rubber to that in Section 3.1 for masticated rubber. All shearing cone results were obtained with the small rotor at 100° C, but on these stiff rubbers the 10 radians per second values are too low because of the temperature rise in the rubber during shearing.

4.1. General behavior of unmasticated smoked sheet

If unmasticated smoked sheet is heated for 1 minute and then sheared at 1 radian per second, a curve similar to the first curve of Figure 1 is obtained, at a higher level of stress, for the first few minutes, but for many samples the curve then begins to rise. Shearing at 10 radians per second for short periods causes subsequent stress readings at 1 radian per second to lie even higher, but prolonged shearing—say 20 minutes for a typical sample—at 10 radians per second causes the sample to begin to soften. The amount of stiffening and the period before softening starts depend on the sample, while some samples start to soften as soon as shearing commences.

The behavior is more interesting if stress/strain-rate curves are obtained after successive periods of shearing at 10 radians per second. The curves in Figure 6 were obtained in this manner, a linear scale being used, for clarity, on the stress axis. Curve 1 was obtained by shearing a sample for 5 minutes at 1.0,

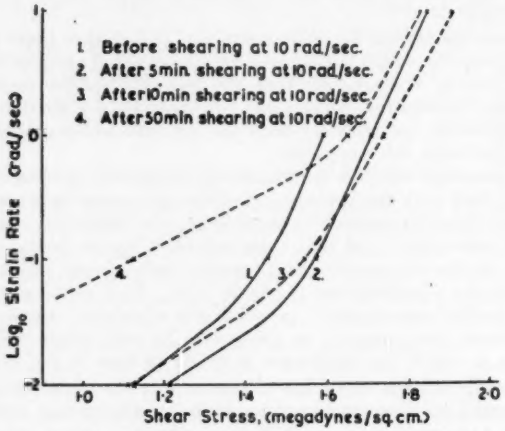


Fig. 6.—Semi-logarithmic stress/strain-rate curves for raw smoked sheet after various periods of shearing at 10 radians per second.

0.1, and 0.01 radian per second successively; the sample was then sheared for 5 minutes at 10, 1.0, 0.1, and 0.01 radians per second successively (curve 2); this sequence was repeated (curve 3), and the sample was then sheared for a further 40 minutes at 10 radians per second before a final sequence of 5 minute runs at the lower rates (curve 4).

The stress/strain-rate curve for the original rubber is very steep, and a small amount of mechanical working (shearing at 10 radians per second) stiffens the sample for tests at all strain rates (curve 2). Further shearing at a high rate makes the rubber stiffer, judged by tests at moderate or high rates, but softer, judged by tests at low rates, making the curve less steep (curve 3). More prolonged shearing at first causes further softening judged by tests at low rates, and finally a general shift of the curve to the left, softening being obvious at all test strain rates (curve 4).

This remarkable behavior is consistent with certain other work. Blow and Wood[16] have reported that mastication of raw rubber in an internal mixer filled

with nitrogen may initially cause a rise in Mooney viscosity, and Hoekstra[17] reported a slight stiffening of crepe rubber in the first minute or two or milling, although this effect apparently disappeared when the samples were stored. Scott and Whorlow[18] have reported that slight milling of smoked sheet during preparation of samples for Williams tests may reduce the Williams value considerably, while having little effect on shearing-cone results at a high strain rate. This might conceivably have been due to porosity in the samples, but it now seems almost certainly due to the wide difference in strain rate between the two types of test.

As mentioned above, the magnitude of the stiffening produced by short high-speed shearing varies considerably from sample to sample, and is not always present.

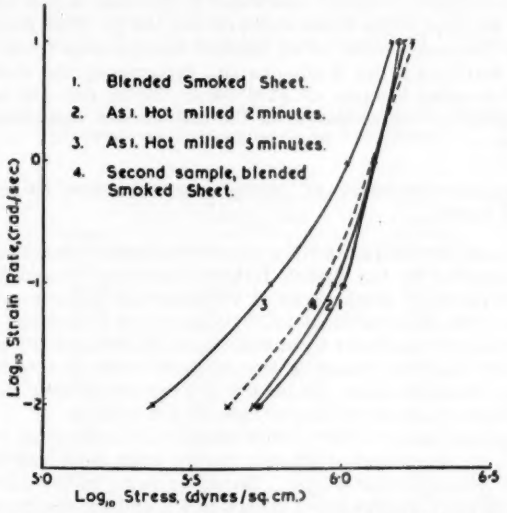


FIG. 7.—Logarithmic stress/strain-rate curves for unmilled and lightly milled blended smoked sheet samples.

It is important to emphasize that some stiffening occurs also on shearing a fresh sample for a long period at 1.0 radian per second, whereas prolonged heating without shearing has little or no effect. It therefore appears that the elevated temperature, particularly the high local temperature which may occur on shearing at the highest rate, is not the cause of the stiffening.

4.2. EFFECT OF MASTICATION OF SMOKED SHEET

It is now convenient to return to a consideration of the earliest stages of mastication of the blended smoked sheet used for the mastication tests discussed in Section 3.2. Figure 7 shows stress/strain-rate curves obtained with the small rotor before mastication and on samples hot milled for 2 or 5 minutes. The samples were sheared for 10 minutes at 1.0 radian per second and then for 10 minutes at 10.0, 1.0, 0.1, and 0.01 radians per second in turn. The curves were obtained from the last four periods of shearing.

The 2-minute milled sample shows signs of stiffening according to tests at high strain rates and softening by tests at low rates, as might be anticipated from the results discussed above, while 5 minutes' milling causes a general softening, not very pronounced at the highest strain rate. The apparent analogy between milling and shearing at a high rate in the plastometer is very interesting, and may be of value in later investigations.

In addition, Figure 7 shows (dotted) the stress/strain-rate curve for the blended smoked sheet used in the duplicate series of mastication tests. It will be recalled that masticated samples from this batch give stress/strain-rate curves which fit into the family formed by the samples from the first batch (Figure 4). As the curves for the two batches before mastication differ markedly (curves 1 and 4, Figure 7), it appears that the form of the curve for samples from different batches masticated in the same way is relatively independent of the form of the initial curve for the batch. This was confirmed by hot milling 150-gram batches of six smoked sheet samples (some of those considered in Section 4.3) for 6 minutes and determining the stress/strain-rate curves. The milled samples all gave curves fitting into the main series in Figure 4, although the properties of the raw smoked sheet samples differed considerably.

4.3. Comparison of tests by various instruments on unmasticated smoked sheet

Results were obtained on thirteen samples of smoked sheet of known Mooney viscosity, supplied by the British Rubber Producers' Research Association. Preliminary results of comparisons of Williams and Mooney values for these samples have been reported previously[19]; it was shown that eleven of the samples fitted fairly closely to a linear regression line of Williams value against Mooney viscosity, but that the remaining two samples—both of a remilled grade of sheet—gave Williams values abnormally low relative to their Mooney values. The results now given throw further light on the position.

Shearing-cone tests at 100° C were carried out in the usual way, using the small rotor, to give stress/strain-rate curves after considerable preliminary shearing at 10 radians per second. However, owing to the differences in behavior for different samples noted in Section 4.1, and the continuous changes in properties which occur during shearing, the curves cannot be regarded as characteristic of the rubbers in the same sense as can curves for masticated rubbers. Nevertheless, they give a useful guide to any major differences between samples.

The first point of interest is whether tests on the shearing-cone plastometer at 1 radian per second are closely correlated with Mooney viscosity determinations, for which the mean rate of strain is of about this value. The second, third, and fourth columns of Table 4 give the Mooney viscosity, the shearing-cone plastometer reading (in arbitrary units) 4 minutes after commencing shearing (at 1 radian per second), and the corresponding reading after a sufficient period of shearing at 10 radians per second to give a reasonably steady value for the 1 radian per second shear stress. Samples are arranged in order of Mooney viscosity.

Agreement between columns 2 and 3 is probably as satisfactory as could be expected. Comparison of columns 3 and 4 gives some indication of the magnitude of the stiffening or softening which rapid shearing may produce in some samples, and shows that there are considerable differences in the behavior of the various samples in this respect.

Column 5 gives the compressed thickness of 1 cc. cylinders after 3 minutes' compression in the Williams plastometer at 100° C. (To prepare the test-pieces, 5-cm. squares of the smoked sheet were heated to 100° C for 10 minutes, plied up to 2 cm. thick, and compressed to 1.2 cm. thick in a press at 100° C; the press was allowed to cool overnight, and cylinders of 1-cc. volume, approximately 1.1×1.1 cm. were cut from the rubber slab). The two samples showing abnormally low Williams values are numbers 35 and 39. The final column of Table 4 gives the shearing cone reading at the lowest rate, 0.01 radian per second. The correlation between columns 5 and 6 is slightly better than between columns 5 and 3 for the 11 samples forming the main group, and sample 39 no longer appears anomalous. Thus the reason for the disagreement between Mooney and Williams results for sample 39 may confidently be taken to be the unusually low slope of the logarithmic stress/strain-rate curve for this sample.

This explanation apparently does not apply to sample 35, which behaved very nearly like sample 37 in the shearing cone instrument. However, sample

TABLE 4

MOONEY, SHEARING-CONE, AND WILLIAMS RESULTS ON THIRTEEN SAMPLES OF UNMASTICATED SMOKED SHEET

Sample number	Mooney value	Shearing-cone reading (1 rad. per sec.) Arbitrary units		Williams 3 min. comp. thickness (mm./100)	Shearing-cone reading 0.01 rad. per sec. Arbitrary units
		4 min.	Steady		
44	53.5	64	62	293	30
41	69.0	86	76	337	42
45	75.0	94	97	400	65
40	81.5	96	100	384	65
36	84.5	100	113	421	72
46	86.0	101	104	403	69
47	90.0	100	110	411	65
39	92.5	102	76	319	35
37	93.0	108	108	410	71
35	101.5	111	113	350	72
38	105.0	124	123	437	87
43	108.5	122	126	461	87
42	111.0	128	135	486	99

35 had a high degree of recovery after the Williams test, showing that the true flow which occurred was not very great, and this may be the cause of the apparent discrepancy between shearing cone and Williams results. Sample 39 did not show unusually high recovery.

It appears, then, that the anomalous behavior of samples 35 and 39 may be due to quite distinct causes. It will be necessary to obtain further data before the interrelationships of Williams compression and recovery data with shearing cone results on unmasticated smoked sheet can be understood. The present preliminary survey will, it is hoped, give some guidance on likely lines of approach.

5. DISCUSSION

5.1 MECHANISMS OF MASTICATION AND PLASTIC FLOW

It is of interest to consider the above results in connection with the theory of mastication recently proposed by Pike and Watson[8]. These authors present convincing evidence that mastication at low temperatures occurs by mechani-

cal rupture of the polyisoprenic chains, the resulting free radicals subsequently recombining, or combining with a "radical acceptor" such as oxygen; or producing chain branching or cross-linking. At higher temperatures, in the presence of air, thermal autoxidative scission is the predominant cause of degradation of molecules.

From this theory, it is probable that rubber masticated at a low temperature contains a larger propertion of branched or cross-linked chains than rubber masticated at a higher temperature to the same degree, as judged, for example, by the stress necessary to shear it at one radian per second. This is consistent with the increased steepness of the strain-rate/stress curve for the cold-milled sample shown in Figure 4. It is likely that mechanical chain scission, followed by radical recombination, also occurs continuously under the substantially oxygen-free conditions of shearing in the cone plastometer, at least at the higher speeds; in a laboratory mill with rolls of 6-inch diameter, running at 20 and 30 r.p.m., respectively, and with a nip of 0.1 inch, the rate of shear in the nip is about 30 radians per second, and Figure 6 shows that the shearing-cone plastometer, running at the higher speeds, will produce stresses almost as great as this rate of shear in the mill. If, therefore, it is assumed that mechanical chain scission can occur in the plastometer, several other results can be explained simply. For example, the stiffening observed in the initial stages of shearing smoked sheet (Figures 6 and 7) may be due to the formation of a few branched or cross-linked chains by the first free radicals formed. The stiffening occurring when the rubber is allowed to rest after shearing (Figure 3) may be due to recombination of free radicals present at the instant shearing ceases, but, alternatively, may be due to the return of molecules to a random disposition after alignment during shearing. Since elastic recovery of masticated rubber at 100° C is substantially complete within 30 seconds[18], the first explanation may be more consistent with the time taken for maximum stiffening to occur. Finally, the cross-links or branched chains supposedly present in the cold-milled samples would be the ones most likely to receive momentarily high stresses, with consequent rupture of the molecules, so that such samples would decrease rapidly in stiffness during the first few minutes of shearing. This agrees with the results reported in Section 3.2.2 (Table 2). Similar behavior has been observed on shearing heavily masticated rubber which has been very lightly cross-linked thermally by heating with di-tertbutyl peroxide. Such rubber shows a very rapid decrease in stress with time during its initial shearing, and subsequently a strain-rate stress curve similar in slope to that of cold-milled smoked sheet. 5.2. Empirical description of rheological behavior.

SUMMARY

Extensive tests on unmasticated and masticated smoked sheet samples in the shearing-cone and Williams plastometers are reported. These constitute a preliminary survey of the behavior of these materials during shearing at various rates and for various periods at elevated temperatures.

Masticated rubber shows a temporary stiffening when kept at normal or elevated temperature; to eliminate this, and so obtain reproducible plasticity measurements, the rubber must be sheared at a high rate. Since normal Mooney and Williams tests do not involve high shear rates, the influence of this stiffening as a possible source of error needs examining.

In tests at 100° C, the logarithmic stress/strain-rate curve is convex to the log stress axis. The most important difference observed between samples

prepared by masticating one batch of smoked sheet in various ways was in the slope of the curve (log stress plotted horizontally), the curves for cold-milled samples being steeper than for samples prepared by hot milling or by mastication in an internal mixer. Curves for samples plasticized in the same way for different periods do not cross. There is evidence that the results of other types of plasticity test can be predicted from the stress/strain-rate curve for the sample. These last two observations, if confirmed by more extensive tests, indicate that for control of normal mastication processes a compression test such as the Williams can be satisfactory, provided the mastication method remains basically the same, that is, using the same type of machine (mill or internal mixer) and similar temperature conditions. The method of mastication appears to be more important than the properties of the raw rubber used as starting material in determining the properties of masticated rubber.

Tests on unmasticated smoked sheet showed that many samples stiffen during shearing or during very light mastication; this effect persists longer, under continued shearing, when stiffness is measured at a high strain rate than when measured at a low rate; in other words, the stress/strain-rate curve becomes much less steep and crosses the curve for very lightly sheared rubber. This latter behavior, apparently not previously observed, is shown to be consistent with certain other observations that have been reported. The complex changes produced by short milling treatments, and which vary from one rubber to another, may be the cause of inconsistencies in Mooney tests on unmasticated rubbers, which are usually prepared for testing by a few passages through a mill. The fact that such treatments may alter the stiffness in different directions according as this is measured at high or low strain rate is doubtless one reason why Mooney and Williams tests on unmasticated rubbers do not correlate closely.

In contrast to this complex and variable behavior, rubbers that have been subjected to a normal mastication treatment give stress/strain-rate curves that do not cross, so tests at one strain rate give a valid indication of their relative behavior at other strain rates. This observation supports the view already held in some quarters that in classifying natural rubbers by a plasticity test they should first be given a standard mastication or shearing treatment.

Many of these conclusions must be regarded as tentative until confirmed on a larger number of rubber samples; with this reservation they form a more complete picture than has hitherto been available of the plastic behavior of unvulcanized raw rubber, which must form the basis for improving control test methods.

REFERENCES

[1] Mooney, *Physics* **7**, 413 (1936); RUBBER CHEM. & TECHNOL. **10**, 214 (1937).
[2] Hamm and van Rossem, *Proc. Intern. Rheol. Congress*, The Hague, **1948**, II, 210.
[3] Saunders and Treloar, *Trans. Inst. Rubber Ind.* **24**, 92 (1948).
[4] Piper and Scott, *J. Sci. Instruments* **22**, 206 (1945).
[5] Williams, *Ind. Eng. Chem.* **16**, 362 (1924).
[6] Piper and Scott, *J. Rubber Research* **16**, 151 (1947).
[7] Scott, *Trans. Inst. Rubber Ind.* **7**, 169 (1931); **10**, 481 (1935).
[8] Pike and Watson, *J. Polymer Sci.* **9**, 229 (1952).
[9] Mooney, *Ind. Eng. Chem. Anal. Ed.* **6**, 147 (1934).
[10] Whorlow, *J. Rubber Research* **20**. 39 (1951); RUBBER CHEM. & TECHNOL. **25**, 387 (1952).
[11] Whorlow, *J. Rubber Research* **18**, 51 (1949); see also Mooney, *Physics* **7**, 413 (1936); RUBBER CHEM. & TECHNOL. **10**, 214 (1937).
[12] Mullins and Whorlow, *Trans. Inst. Rubber Ind.* **27**, 55 (1951).
[13] Piper and Scott, *J. Rubber Research* **17**, 135 (1948).
[14] Treloar, *Trans. Inst. Rubber Ind.* **25**, 167 (1949).
[15] Scott, RUBBER CHEM. & TECHNOL. **18**, 877 (1945).
[16] Blow and Wood, *Trans. Inst. Rubber Ind.* **25**, 309 (1950).
[17] Hoekstra, *Proc. Rubber Technol. Conf. London*, **1938**, p. 362.
[18] Scott and Whorlow, *India-Rubber J.* **125**, 135 (1953).
[19] Whorlow, *India-Rubber J.* **120**, 658 (1951).

RELAXATION TIME SPECTRUM, ELASTICITY, AND VISCOSITY OF RUBBER.* I

W. KUHN, O. KÜNZLE, AND A. PREISSMANN

PHYSICAL-CHEMICAL INSTITUTE, UNIVERSITY OF BASEL, BASEL, SWITZERLAND

NATURE OF THE PROBLEM

Qualitative basis for the occurrence of a relaxation time spectrum[1]

Work on the relation between the viscous and elastic properties of amorphous materials several years ago[2] showed that a large number of processes in the mechanical deformation of a medium may be expected to occur, which are more or less independent of one another, especially when the medium contains linear high polymers. When such a material is deformed and maintained in this state, then, as has been shown[3], a change of the form of a linear molecule occurs, which is partly a change of the state of probability. As a result of this deformation, there is a restoring force which is partly of an elastic kind and partly of a probability nature.

These changes of form disappear partially or entirely by relaxation if the experimental body is held at constant elongation, when the linear segments possess a certain mobility relative to one another. The extent to which the molecular segments must travel relative to one another or relative to their surroundings to re-establish a "normal" state varies widely in any one high polymer material. The range of travel depends on whether changes of distance of neighboring atoms or changes of distance between more distant parts of the molecule or even changes of the shape of the entire molecule are considered. Correspondingly, the relaxation times of that portion of the stresses corresponding to the smaller or greater changes in distances, produced by a sudden deformation of the material, will vary widely. In high-molecular substances, many restoring force mechanisms[4] acting in parallel with relaxation times lying far from one another may be expected, *i.e.*, there is a wide spectrum of relaxation times.

Definition of partial moduli of elasticity and associated relaxation times; continuous relaxation times spectrum

This relation can be described quantitatively by the statement that the stress σ (restoring force per sq. cm. of the expanded body), which is observed when the experimental body of length l is quickly expanded to length $l + \Delta l$, and then is kept at that length, $l + \Delta l$, can be represented as follows:

$$\sigma = \frac{\Delta l}{l} \cdot \sum_i E_{i0} e^{-t/\tau_i} \qquad (1)$$

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Mark Dannis and Myrtle Watson of the B. F. Goodrich Research Center, Brecksville, Ohio, with assistance from the authors. Part I is from *Helvetica Chimica Acta*, Vol. 30, No. 1, pages 307–328 (1947); Part II is from *Helvetica Chimica Acta*, Vol. 30, No. 2, pages 464-486 (1947).

Using for the modulus of elasticity, E, the usual definition:

$$\frac{\sigma}{\Delta l/l} = E \tag{2}$$

there is obtained from Equation (1):

$$E(t) = \sum_i E_{i0} e^{-t/\tau_i} \tag{2a}$$

There is thus obtained a modulus of elasticity which depends on the time t (time between the change of length Δl and the measurement of the stress σ). The value E_{i0} in (2a) has been designated[5] as the fundamental value of the individual partial elastic modulus, and τ_i as the corresponding relaxation time. The sums in (1) or (2a) are to extend over the total of the individual partial elastic moduli occurring in the substance. Even in simple substances, such as propyl alcohol, as has been shown[6], several partial elastic mechanisms exist; the high molecular materials differ from the low by a very much larger range of the E_{i0}, τ_i spectrum.

Still better than the representation by an ultimate number of discrete partial elasticity moduli is an expression for E which depends on the time t, and obtained when the sum in (2) is substituted by an integral, *i.e.*, calculated with a continuous relaxation time spectrum. Thus there is obtained[6]

$$E(t) = \int_0^\infty \frac{dE_0}{d\tau} e^{-t/\tau}\, d\tau \tag{3}$$

Since the sum in (2a) has to be extended over all existing values of E_{i0} and τ_i, wherein some of the relaxation times may be very short, while others may be very long, the integral (3) will, in general, extend over all values of τ from $\tau = 0$ to $\tau = \infty$. $dE_0/d\tau$ the fraction of the fundamental value of the modulus contributed by an interval $d\tau = 1$, taken in the region of a particular value τ is evidently a function of τ, *i.e.*, the distribution density of the fundamental values of the modulus at the point τ. These can be very small in some locations and at others assume very large values.

For $t = 0$, *i.e.*, for the case when the stress is measured immediately after very fast deformation of the experimental body, (2a) changes to:

$$E = E_0 = \Sigma E_{i0} \tag{4}$$

Summation role for the fundamental values of the partial elastic moduli

It has been shown[3] that the sum E_0 (*i.e.*, ΣE_{i0}) is found to have, for various materials, values of the same order of magnitude, namely, about $10^{10} - 10^{12}$ dynes per sq. cm.

According to (3) this means:

$$\int_0^\infty \frac{dE_0}{d\tau}\, d\tau = E_0 \cong 10^{10} - 10^{12} \text{ dynes per sq. cm.} \tag{4a}$$

E_{i0} in Equation (4), or the value of E_0 in (4) or (4a), depends only slightly on temperature. The known temperature sensitivity of visco-mechanical behavior is connected with the strong temperature dependence on relaxation time[3]. At low temperatures, all the relaxation times are very large; at higher temperatures they become smaller; obviously, however, the transition of large

to small τ values does not necessarily occur at any one temperature for the various restoring force mechanisms.

Vulcanized rubber represents a special case, inasmuch as the relaxation times for almost all of the internal restoring force mechanisms are very small. The time τ is practically infinitely large for one particular internal mechanism, namely, for that portion of the restoring force which results from the improbable configuration of the filaments contained in distorted network[7].

Description of elastic behavior with the concept of relaxation time spectrum

As learned from (2) and (3), the elastic behavior of a given material can be fully predicted as soon as the relaxation time spectrum, *i.e.*, the value of E_{i0} and τ_i in (2a) or the value $dE_0/d\tau$ in (3), is given as a function of τ.

Extension forces.—For example, when all E_{i0} and τ_i are given, the stress σ existing in a test-piece at a moment t_1 can be given if the test-piece has been deformed during the time interval $t = 0$ to t_1 with an arbitrarily chosen velocity function:

$$\frac{d}{dt}\left(\frac{\Delta l}{l}\right) = \frac{d\alpha}{dt} \tag{5}$$

Thus, on the basis of Equation (1), the stress produced in the test-piece in a time interval dt at the moment t is, at this very moment, equal to:

$$\frac{d\sigma}{dt}\,dt = \frac{d\alpha}{dt}\,dt\Sigma E_{i0} \tag{6}$$

and this portion of the stress in the interval t to t_1 decreases according to Equation (2a) to:

$$d\sigma = \frac{d\alpha}{dt}\,dt\Sigma E_{i0}e^{-(t_1-t)/\tau_i} \tag{6a}$$

The total stress σ at the moment t_1 is equal to the integral of Equation (6a) taken between the limits 0 and t:

$$\sigma_{t_1} = \int_0^{t_1} \frac{d\alpha}{dt}\left(\sum_i E_{i0}e^{-(t_1-t)/\tau_i}\right) dt \tag{7}$$

Introducing the concept of the continuous relaxation time spectrum, (3), (7) then becomes:

$$\sigma_{t_1} = \int_0^{t_1} \frac{d\alpha}{dt}\left(\int_0^{\infty} \frac{dE_0}{d\tau}\,e^{-(t_1-t)/\tau}\,dt\right) dt \tag{8}$$

It is obvious that σ_{t_1} is, indeed, determined quantitatively by (7) or (8), *i.e.*, that the stress at the time t_1 is determined by the relaxation time spectrum as soon as the deformation rate $d\alpha/dt$ is given as a function of t between 0 and t_1.

Shearing forces.—It had been shown[3] further that, in addition to the elastic behavior, the viscous behavior of a material is determined by the relaxation time spectrum. The proof has been carried out completely[5], but with assumptions which are somewhat more restricted than absolutely necessary. Subsequently, a number of authors have presented their points of view[8] in papers based on this work. Later reference will be made to several further papers dealing with relaxation time spectra.

It is important for the valuation and use of the equation which will be derived not to burden the fundamentals with unnecessary assumptions. There is

given, therefore, in the following, as free as possible from special assumptions, derivations of the more important elementary relationships necessary for the final considerations. Several of these relations are covered by results already obtained[3] or by results which were obtained by the above mentioned authors. It should be mentioned, *e.g.*, that Equation (16a) for the restoring force, and Equation (21) for the viscosity have been derived by J. D. Ferry[9], assuming a distribution of parallel restoring-force mechanisms and used for determining the partial elasticity moduli and relaxation times.

For the following, it is not necessary to assume that restoring force mechanisms working truly parallel to one another exist in any given material; but rather to assume that mechanisms acting in parallel and in series are united in an arbitrarily complicated way to form a system in which the restoring force occurring in a quickly applied change of length can formally be represented by (2a) or (3). It will be shown in a subsequent paper[10] that it is always possible indeed to represent any such system by (2a).

A complicated system of coupled elastic springs arranged partly in series and partly in parallel and retarded by friction mechanisms is thus fully equivalent to a system of elastic springs, each carrying a friction mechanism and all acting in parallel. In the following, when restoring-force mechanisms are mentioned, whose relaxation times lie between τ and $\tau + d\tau$, it should be emphasized that, as far as the model is concerned, the mechanism is not to be taken too literally. This portion of the stress should simply be thought of as decreasing with a relaxation time τ to $\tau + d\tau$, leaving the question open whether these stress decays are related to independent restoring force mechanisms working parallel to each other, or whether they are brought about in a complicated way by mechanisms working partly in series, partly in parallel.

Calculation of viscosity actually amounts to a special case of the description of mechanical elastic behavior, representing in one sense a generalization, in another sense a specialization of (8).

In order to develop this idea, consider a test-piece consisting of a cube 1 cm. on the edge made from the experimental material. The base plane of the cube may be kept at rest while the surface opposite to it is moved in a direction parallel to the base plane with a velocity of $d\gamma/dt$. In order to prevent later repetitions, first assume that $d\gamma/dt$ from $t = 0$ is an arbitrarily assigned function of the time t.

Find the force acting on 1 sq. cm. of the moving plane at moment t. If μ is the Poisson ratio, then the force dF which is produced by the shear $d\gamma = dt \cdot d\gamma/dt$ originating in the interval dt, will in a manner analogous to (6) be:

$$dF = \frac{dF}{dt} \cdot dt = \frac{d\gamma}{dt} \cdot dt \, \frac{1}{2(1+\mu)} \Sigma E_{i0} \tag{6b}$$

This tangential force decreases in the interval t to t_1 by relaxation to:

$$dF = \frac{1}{2(1+\mu)} \frac{d\gamma}{dt} \, dt \Sigma E_{i0} e^{-(t_1 - t)/\tau_i} \tag{8b}$$

(analogous to 6a), and the shearing force at moment t_1 is then (analogous to 8):

$$F_{t_1} = \int_0^{t_1} \frac{1}{2(1+\mu)} \frac{d\gamma}{dt} \left[\Sigma E_{i0} e^{-(t_1 - t)/\tau_i} \right] dt \tag{9}$$

Depending on the assumption made with respect to the arbitrarily chosen function $d\gamma/dt$ as well as on t_1 and τ_i, there is obtained on the basis of (9) either

the Newtonian viscosity on one hand or the dynamic viscosity and the dynamic torsion modulus on the other hand.

Newtonian viscosity

From (9) there is obtained the common or Newtonian viscosity when $d\gamma/dt$ in the interval 0 to t_1 is made constant, and at the same time t_1 is assumed to be very large in comparison to the largest τ_i value which occurs in the relaxation time spectrum.

When $d\gamma/dt$ is constant, (9) becomes:

$$F_{t_1} = \frac{1}{2(1+\mu)}\frac{d\gamma}{dt}\int_0^{t_1}\left[\Sigma E_{i0}e^{-t_1/\tau_i}\,e^{t/\tau_i}\right]dt = \frac{1}{2(1+\mu)}\frac{d\gamma}{dt}$$

$$\times\left[\Sigma E_{i0}\tau_i e^{-t_1/\tau_i}\,e^{t/\tau_i}\right]_0^{t_1} = \frac{1}{2(1+\mu)}\frac{d\gamma}{dt}\left[\Sigma E_{i0}\tau_i - \Sigma E_{i0}\tau_i e^{-t_1/t_i}\right] \quad (9a)$$

and when the assumption $\tau_i \ll t_1$ is fulfilled, this becomes:

$$F_{t_1} = \frac{1}{2(1+\mu)}\frac{d\gamma}{dt}\Sigma E_{i0}\tau_i \quad (10)$$

The force which acts on 1 sq. cm. of the moving surface is thus independent of t_i if a constant flow rate is maintained during a period t_1, which is greater than any occurring relaxation time τ_i.

The same is, as is well known, characteristic of a so-called Newtonian liquid, the viscosity η of such a liquid being defined by the equation:

$$F = \eta\frac{d\gamma}{dt} \quad (11)$$

Equating (10) and (11) gives:

$$\eta = \frac{1}{2(1+\mu)}\sum_1 \tau_i E_{i0} \quad (12)$$

For materials, such as rubber, for which the volume of the test-piece remains unchanged in deformation, the Poisson number $\mu = 0.5$. Equation (12) then becomes:

$$\eta = \tfrac{1}{3}\Sigma\tau_i E_{i0} \quad (\text{for } \mu = 0.5) \quad (12a)$$

The viscosity is thus determined entirely by the relaxation period spectrum. (12) and (12a) are identical with equations already given[3].

If the relaxation time spectrum is represented by the smooth distribution (3) instead of the stepped distribution (2), then instead of (12), the following expression is obtained:

$$\eta = \frac{1}{2(1+\mu)}\int_0^{\tau_1'}\frac{dE_0}{d\tau}\tau d\tau \quad (13)$$

It must, therefore, be assumed that the relaxation time spectrum has an upper limit τ'_1 and, that t_1, the time between the beginning of the flow process and the measurement of the shearing force (9), is much greater than τ'_1. This condition corresponds to the assumption made in the establishment of (12) that t_1 be much larger than the largest of the relaxation times τ_i occurring in the spectrum.

If the condition that t_1 be much larger than the largest of the relaxation times present is not filled, then a constant viscosity observable from the flow cannot be obtained.

When $d\gamma/dt$ is held constant between $t = 0$ and $t = t_1$, (9a) is still valid, but the second term of the summation on the right side of the last equation in (9a) no longer vanishes; the shearing force is then dependent on t_1, as is also the viscosity which has to be assigned to the substance on the basis of a comparison of (9a) and (11).

Now consider the contribution to F_{t_1} derived from a restoring force mechanism (perhaps with an index k) in which $\tau_k \gg t_1$. According to (9a) this becomes:

$$(F_{t_1})_{\text{contribution } k} = \frac{1}{2(1+\mu)}\frac{d\gamma}{dt}\left[\tau_k E_{k_0} - \tau_k E_{k_0} e^{-t_1/\tau_k}\right] \simeq \frac{1}{2(1+\mu)}\frac{d\gamma}{dt} \times \left[\tau_k E_{k_0} - \tau_k E_{k_0}\left(1 - \frac{t_1}{\tau_k}\right)\right] = \frac{1}{2(1+\mu)}\frac{d\gamma}{dt}\, t_1 E_{k_0} \quad (14)$$

This is nothing but the mechanical stress which is produced, according to (6b), in this mechanism when no relaxation occurs, if during the time t_1 a constant flow rate $d\gamma/dt$ is maintained. As has been discussed fully[2], this signifies that the restoring force mechanisms for which $\tau \ll t_1$ contribute essentially to the viscosity, and those for which $\tau \gg t_1$ to the elasticity. For further details and conclusions see the earlier work[3].

Dynamic elastic and shearing modulus and dynamic viscosity

When individual relaxation times τ_i are of the same order of magnitude as the experimental time t_1 taken for the measurement of elasticity or viscosity, an elastic modulus (dynamic) independent of t_1 and also of a well defined (dynamic) viscosity (which is likewise independent of t_1) can be obtained only if in Equations (8) and (9), there is introduced in each case a periodic function of the time t in the interval 0 to t_1 for the arbitrary rate of deformation $d\alpha/dt$ or the shearing rate $d\gamma/dt$.

If the shearing deformation γ of the cube considered in the preceding section would be equal to:

$$\gamma = \gamma_0 \cdot \sin \omega t \quad (15)$$

$$\frac{d\gamma}{dt} = \gamma_0 \cdot \omega \cdot \cos \omega t \quad (15a)$$

The contribution of a restoring force mechanism with an index k to the shearing force F_{t_1} at a moment t_1 then becomes according to (9):

$$(F_{t_1})_{\text{contribution } k} = \frac{1}{2(1+\mu)}\int_0^{t_1} \gamma_0\omega \cos \omega t \cdot E_{k_0} \cdot e^{-(t_1-t)/\tau_k}\, dt = \frac{e^{-t_1/\tau_k}}{2(1+\mu)}\gamma_0\omega E_{k_0}\left[\frac{\frac{1}{\tau_k}e^{t/\tau_k}\cos \omega t + \omega e^{t/\tau_k}\sin \omega t}{\left(\frac{1}{\tau_k}\right)^2 + \omega^2}\right]_0^{t_1} = \frac{\gamma_0 \cdot \omega \cdot E_{k_0}}{2(1+\mu)}\frac{\frac{1}{\tau_k}\cos \omega t + \omega \sin \omega t}{\left(\frac{1}{\tau_k}\right)^2 + \omega^2} - \frac{\gamma_0\omega E_{k_0}}{2(1+\mu)}\frac{\frac{1}{\tau_k}e^{-t_1/\tau_k}}{\left(\frac{1}{\tau_k}\right)^2 + \omega^2} \quad (16)$$

When the time t_1 between the beginning of the periodic displacement and the moment of measuring the strain is large in comparison to the period $T = 2\pi/\omega$, *i.e.*, when after a large number of cycles the last member of (16) is very small in comparison to other members, then there is obtained:

$$(F_{t_1})_{\text{contribution } k} = \frac{\gamma_0 \cdot \omega E_{k_0}}{2(1+\mu)} \frac{\frac{1}{\tau_k}\cos \omega t + \omega \sin \omega t}{\left(\frac{1}{\tau_k}\right)^2 + \omega^2} \tag{16a}$$

The mechanical energy, which is applied per sq. cm. of the material on the basis of the restoring force mechanisms with an index k during the displacement period (time t_1 to $t_1 + 2\pi/\omega$), is given from (15a) and (16a) as:

$$\left(\overline{\frac{dA}{dt}} \cdot \frac{2\pi}{\omega}\right)_{\text{contribution } k} = \omega^2 \gamma_0^2 \frac{E_{k_0}}{2(1+\mu)} \cdot \frac{1}{\omega \tau_k} \times \int_0^{2\pi/\omega} \frac{\cos^2 \omega t \cdot dt \cdot \omega}{\left(\frac{1}{\tau_k}\right)^2 + \omega^2} = \omega \cdot \gamma_0^2 \frac{E_{k_0}}{2(1+\mu)} \frac{\pi \cdot \frac{1}{\tau_k}}{\left(\frac{1}{\tau_k}\right)^2 + \omega_2} \tag{17}$$

The average work performed per sq. cm. and per second is obtained when this is multiplied by $\omega/(2\pi)$, thus:

$$\left(\overline{\frac{dA}{dt}}\right)_{\text{contribution } k} = \omega^2 \frac{\gamma_0^2 E_{k_0}}{2(1+\mu)} \frac{1}{2\tau_k} \frac{1}{\left(\frac{1}{\tau_k}\right)^2 + \omega^2} = \frac{\omega^2 \gamma_0^2 E_{k_0}}{2 \cdot 2(1+\mu)} \cdot \frac{\tau_k}{\omega^2 \tau_k^2 + 1} \tag{18}$$

By the summation of all k values, there is obtained the actual work converted into heat per sq. cm. per second due to shear (15):

$$\overline{\frac{dA}{dt}} = \frac{\omega^2 \gamma_0^2}{2} \cdot \frac{1}{2(1+\mu)} \sum_i \frac{E_{i_0} \cdot \tau_i}{\omega^2 \tau_i^2 + 1} \tag{19}$$

For a medium possessing the viscosity η, on the basis of (11) and (15a):

$$\overline{\frac{dA}{dt}} = \left(\overline{F \cdot \frac{d\gamma}{dt}}\right) = \eta \cdot \overline{\left(\frac{d\gamma}{dt}\right)^2} = \frac{\omega^2 \gamma_0^2}{2} \cdot \eta \tag{20}$$

Combining (19) and (20) gives:

$$\eta = \frac{1}{2(1+\mu)} \sum_i \frac{E_{i_0} \tau_i}{\omega^2 \tau_i^2 + 1} \tag{21}$$

of, if a continuous relaxation time spectrum (3) is used instead of a discontinuous one (2), then:

$$\eta = \frac{1}{2(1+\mu)} \int_0^\infty \frac{dE_0}{d\tau} \frac{\tau}{\omega^2 \tau^2 + 1} d\tau \tag{22}$$

The relationships of (21) and (22) represent a generalization of the relations (12) and (13) for the case where the relaxation time spectrum is not vanishing already in the region of relaxation times τ, which are short in comparison to the flow duration. Conversely, (21) and (22) are converted to (12) and (13) when the largest of the relaxation times τ_i are small in comparison to the duration of the displacement time $2\pi/\omega$ caused in the viscosity measurement according to (15). For $\tau \ll 1/\omega$ or $\omega\tau \ll 1$, $\omega^2\tau^2$ can be neglected in comparison to 1 in the denominator of (21) and (22).

(21) and (22) show that the viscosity η established by measuring the damping of a periodic displacement generally depends on the angular velocity ω of the displacement, but that this frequency dependence is determined completely by the relaxation time spectrum (Equation 1 or 3).

In cases where the test-piece is periodically deformed by elongation instead of shear, with the relative change in length (5) equal to:

$$\alpha = \alpha_0 \cdot \sin \omega t \tag{23}$$

a derivation entirely analogous to that given above is obtained by the mechanical energy converted into heat per cc. per second:

$$\overline{\frac{dA}{dt}} = \frac{\omega^2\alpha_0^2}{2} \sum_i \frac{E_{i_0}\tau_i}{\omega^2\tau_i^2 + 1} \tag{24}$$

Or for the case of continuous relaxation time spectrum:

$$\overline{\frac{dA}{dt}} = \frac{\omega^2\alpha_0^2}{2} \int_0^\infty \frac{dE_0}{d\tau} \frac{\tau}{\omega^2\tau^2 + 1}\, d\tau \tag{25}$$

In the foregoing, the work converted into heat per second for each individual restoring force mechanism has been calculated, and therefore the total frictional energy has been determined by summation, and hence the viscosity.

Instead of this, the total (resultant) force could be compiled, taking into account the phases of the partial forces (16a), and the total force against the motion (15) with the phase displacement, ϕ, obtained, and finally the work output from the total force and this phase displacement could be calculated.

For a shear deformation occurring periodically according to (15), the total stress is obtained by summation of (16a) for all τ values:

$$F_{t_1} = \frac{\omega \cdot \gamma_0}{2(1+\mu)} \sum_k E_{k_0} \frac{\frac{1}{\tau_k} \cos \omega t_1 + \omega \sin \omega t_1}{\left(\frac{1}{\tau_k}\right)^2 + \omega^2} \tag{26}$$

or for a continuous relaxation spectrum:

$$F_{t_1} = \frac{\omega \cdot \gamma_0}{2(1+\mu)} \int_0^\infty \frac{dE_0}{d\tau} \frac{\left(\frac{1}{\tau}\right) \cos \omega t_1 + \omega \sin \omega t_1}{\left(\frac{1}{\tau}\right)^2 + \omega^2}\, d\tau \tag{26a}$$

If the shear and shear velocity according to (15) and (15a) are substituted in this equation, there is obtained:

$$F_{t_1} = \gamma \cdot \frac{\omega^2}{2(1+\mu)} \int_0^\infty \frac{dE_0}{d\tau} \frac{d\tau}{\left(\frac{1}{\tau}\right)^2 + \omega^2} + \frac{d\gamma}{dt} \frac{1}{2(1+\mu)} \int_0^\infty \frac{dE_0}{d\tau} \frac{\frac{1}{\tau} d\tau}{\left(\frac{1}{\tau}\right)^2 + \omega^2} \quad (27)$$

The first term of the sum, proportional to the deformation γ, can be interpreted as a portion following Hooke's law (proportionality between stress and deformation) and the second as following Newton's law of viscosity (proportionality between stress and rate of deformation). The proportionality constants represent respectively the (dynamic) torsion modulus, $G(\omega)$, *viz.*, the (dynamic) elastic modulus, $E(\omega)$ and the (dynamic) viscosity coefficient, $\eta(\omega)$. Thus:

$$E(\omega) = 2(1+\mu)G(\omega) = \omega^2 \int_0^\infty \frac{dE_0}{d\tau} \frac{\tau^2 d\tau}{1+\omega^2\tau^2} \quad (28)$$

$$\eta(\omega) = \frac{1}{2(1+\mu)} \int_0^\infty \frac{dE_0}{d\tau} \frac{\tau d\tau}{1+\omega^2\tau^2} \quad (29)$$

These are obviously all functions of the frequency ω of motion. Equation (29) is identical to Equation (22), derived in the preceding section in a somewhat different way.

The stress F_{t_1}, Equation (27), can be represented as a sine function displaced in phase against deformation (15):

$$F_{t_1} = \frac{\gamma_0 \cdot \omega^2}{2(1+\mu)} \sqrt{\frac{1}{\omega^2}\left(\int_0^\infty \frac{dE_0}{d\tau} \frac{\tau d\tau}{1+\omega^2\tau^2}\right)^2 + \left(\int_0^\infty \frac{dE_0}{d\tau} \frac{\tau^2 d\tau}{1+\omega^2\tau^2}\right)^2} \times \sin(\omega + \varphi)t \quad (30)$$

For phase displacement ϕ between deformation and stress:

$$\tan\varphi = -\frac{1}{\omega} \frac{\int_0^\infty \frac{dE_0}{d\tau} \frac{\tau d\tau}{1+\omega^2\tau^2}}{\int_0^\infty \frac{dE_0}{d\tau} \frac{\tau^2 d\tau}{1+\omega^2\tau^2}} = -\frac{2(1+\mu)\eta(\omega)}{E(\omega)} \quad (31)$$

Since, as soon as the relaxation time spectrum is known, the elastic and viscous properties can be completely summarized according to these relationships, the practical determination of this spectrum presents an important problem.

Attempts to describe the behavior of high polymer substances with the aid of a limited number of restoring force mechanisms

The attempts hitherto undertaken in specific cases to establish the relaxation time spectrum were in each case an attempt to describe the elastic and viscous

behavior of rubber by assuming a limited numer of discrete values E_{i0} with the pertinent relaxation time. As an example, Kuhn in 1939 made the statement that, for soft vulcanized rubber, the first approximation[3] was:

$$E_{10} = 10^6 - 10^7 \text{ dynes/cm}^2 \qquad \tau_1 = \infty$$
$$E_{20} = 10^{11} \text{ dynes/cm}^2 \qquad \tau_2 = 10^{-5} \text{ sec}$$

This tentative description takes into account the fact that soft vulcanized rubber has a static elastic modulus (modulus measured a long time after deformation) of $10^6 - 10^7$ dynes per sq. cm., whereas ΣE_{i0} must, according to (4) and (4a), be about 10^{11} dynes per sq. cm. and η, according to Van der Wyk[11], about 10^6 poises. This description with only two partial elasticity moduli is very crude. The observations made by Hauk and Newmann[12], wherein the strain observed in rubber a few seconds after deformation is noticeably decreased by relaxation, show, as already indicated[3], that relaxation times are present having magnitude of several seconds, in addition to the two relaxation times mentioned above.

An improved equation which takes this and further observations into consideration and describes the behavior of rubber through four groups of relaxation times have been given by Haegel[13]. For rubber:

$$E_{10} = 10^6 - 10^7 \text{ dynes/sq. cm.} \qquad \tau = \infty$$
$$E_{20} = 10^2 - 10^6 \text{ dynes/sq. cm.} \qquad \tau_2 = 10 - 10^{-4} \text{ sec.}$$
$$E_{30} = 10^7 - 10^8 \text{ dynes/sq. cm.} \qquad \tau_3 = 10^{-3} - 10^{-4} \text{ sec.}$$
$$E_{40} = 10^{11} - 10^{12} \text{ dynes/sq. cm.} \qquad \tau_4 = 10^{-13} \text{ sec.}$$

According to experiments by Grün and Haegel[14] on the velocity with which the refraction (birefringence) in quickly elongated rubber samples decays, the behavior could be described still more accurately if the following group was resolved. $E_{20} = 10^2 - 10^6$ dynes per sq. cm., $\tau_2 = 10 - 10^{-4}$ second, into 2 sub-groups $E'_{20} = 2 \times 10^3$ dynes per sq. cm., $\tau_2^{\text{I}} = 1.6 \times 10^{-2}$ sec., $E''_{20} = 1 \times 10^6$ dynes per sq. cm., $\tau_2^{\text{II}} = 4 \times 10^{-3}$.

Here it is emphasized that the description by a discrete $E_{i0} - \tau_i$ spectrum is a help in certain cases, and that an exact discription can be obtained only by a continuous distribution function according to Equation (3).

DETERMINATION OF THE RELAXATION TIME SPECTRUM FROM THE FLOW CURVE

The possibility of calculating the relaxation time spectrum from the flow curve has been mentioned several times. Simha[15], for example, gives a procedure for the conversion without, however, applying it to experimentally determined flow curves. Moreover, Alfrey and Doty[16] also give a method of approximation. At the same time, they indicated the fundamental equivalence of the description of visco-elastic behavior by the flow curve, the relaxation spectrum and other methods.

Empirical equation of the flow (creep) curve

One possibility of finding an empirical continuous distribution function for rubber and several other high elastic substances results from observations of Brenschede[17]. In Brenschede's experiments, the relative change in length $\Delta l/l$ is established as a function of t when the test specimen is, from $t = 0$, subjected to a constant load σ.

Analogous to Equation (2), an elastic modulus E' derived from the flow (creep) experiment can be defined by the relationship:

$$E' = \frac{\sigma}{\frac{\Delta l}{l}} = \frac{\sigma}{\alpha} \tag{32}$$

While in definition (2), $\Delta l/l$ is held constant in time after rapid elongation, and the stress σ depends on time, Equation (1), in this definition (32) the elongating stress σ is to be held constant while $\Delta l/l$ depends on time. The definitions are not exactly identical with one another.

Brenschede established that $\Delta l/l\sigma$, that is, the reciprocal value of modulus E' defined in (32) over a range of time t spanning about six decades, namely:

$$10^{-2} \text{ sec.} < t < 10^{4} \text{ sec.} \tag{33a}$$

can be represented by the expression:

$$\frac{1}{E'} = \frac{a + \ln t}{b} \tag{33}$$

Here a and b are numerical constants. Their values for several substances examined by Brenschede are given in Table I[18].

TABLE I

	a	b (dynes per sq. cm.)	$\ln c$	c (sec^{-1})
Perbunan	13.4	0.9×10^9	12.8	3×10^5
Buna-SS	21	1.7×10^9	20.4	10^9
Buna-S/SS	21	2.2×10^9	20.4	10^9
Natural rubber vulcanizate, loaded	80	4.0×10^9	79.4	10^{35}
Natural rubber vulcanizate, pure (after several measurements)	15	0.1×10^9	14.4	3×10^6

In the foregoing it has been established that the mechanical behavior is determined by the relaxation time spectrum. The reverse problem now appears to be to calculate the relaxation time spectrum from the mechanical elastic behavior, considered as known and represented according to Equation (33). This is essentially a mathematical problem.

Representation of the flow curve by a function of time t, remaining finite from $t = 0$

First of all, in Equation (33), the magnitude $1/E'$ is well defined in the practical experimental range, but fails at $t = 0$. In order not to get into mathematical difficulties by the function (33) becoming infinite when $t = 0$, it may be modified in such a way that it is finite and continuous for $t = 0$ by putting

$$\frac{1}{E'} = \frac{a + \ln t - Ei(-ct)}{b} \tag{34}$$

or according to (32):

$$\alpha = \frac{\sigma}{E'} = \frac{\sigma}{b}[a + \ln t - Ei(-ct)] \tag{34a}$$

wherein

$$-Ei(-x) = \int_x^\infty \frac{e^{-u}}{u}\,du \quad \text{Log integral (Listed in Jahnke-Emde)} \tag{35}$$

and

$$\ln c = a - \ln \epsilon \tag{35a}$$

as

$$\epsilon = 1.781\,;\ln \epsilon = 0.577 \text{ (Euler Constant)} \tag{35b}$$

Function (34) remains finite for $t = 0$, which can be proved by making a series of the function $E_i(-ct)$. Moreover, for small values of t, and in any case in the total range of (33a) for which practical measurements exist, (34) becomes equivalent to (33).

Based on (34a) there is obtained:

$$\frac{d\alpha}{dt} = \frac{\sigma}{b}\cdot\frac{1 - e^{-ct}}{t} \tag{36}$$

a relation from which it can be immediately recognized that $d\alpha/dt$ remains finite for $t = 0$, while for large values of t it changes into the relation resulting from (32) and (33), namely:

$$\frac{d\alpha}{dt} = \frac{\sigma}{b}\cdot\frac{1}{t} \qquad \text{(for large values of } t\text{)} \tag{37}$$

Calculation of the relaxation time spectrum

If the rate of deformation (36) is substituted in (8), there is obtained the stress which exists in a body deformed with this velocity:

$$\sigma(t_1) = \int_0^{t_1} \frac{\sigma}{b}\cdot\frac{1 - e^{-ct}}{t}\left[\int_0^\infty \frac{dE_0}{d\tau}\,e^{-(t_1 - t)/\tau}\,d\tau\right] dt \tag{38}$$

Providing Equation (36) is regarded as an exact expression for the rate of deformation of test samples under constant load, the stress $\sigma(t_1)$ in (38) must be of a magnitude independent of time t_1, thus:

$$\int_0^{t_1} \frac{\sigma}{b}\cdot\frac{1 - e^{-ct}}{t}\left[\int_0^\infty \frac{dE_0}{d\tau}\,e^{-(t_1 - t)/\tau}\,d\tau\right] dt = \text{const.} \tag{38a}$$

The value of the integral (38) depends essentially on the choice of the function $(dE_0/d\tau)(\tau)$, and, in general, depends on t_1. There can be found a definite function $(dE_0/d\tau)(\tau)$ for which the integral (38) no longer depends on t_1 and which thus satisfies Equation (38a). This condition makes possible the determination of this function, and thereby the establishment of the relaxation time spectrum.

In order to solve this problem, put

$$\frac{d\alpha}{dt} = \alpha'(t) \tag{39}$$

where, $\alpha'(t)$ is the function given in (36). Now write (3) as:

$$\int_0^\infty \frac{dE_0}{d\tau}\,e^{-(t_1 - t)/\tau}\,d\tau = E(t_1 - t) \tag{40}$$

Equation (38) then becomes:

$$\sigma(t_1) = \int_0^{t_1} \alpha'(t)E(t_1 - t)dt \tag{41}$$

As soon as $\sigma(t_1)$ and $\alpha'(t_1)$ are determined experimentally between $t = 0$ and $t = t_1$, it is possible to determine $E(t)$, *i.e.*, the relaxation time spectrum (3).

For better distinction of the variable, put x in place of t in (41). The equation then reads:

$$\sigma(t_1) = \int_0^{t_1} \alpha'(x)E(t_1 - x)dx \tag{41a}$$

Now multiply (41a) by $e^{-t_1 s}$, where s is a newly introduced working variable; then it is possible to integrate over t_1 from 0 to ∞.

$$\int_0^{\infty} e^{-t_1 s}\,\sigma(t_1)dt_1 = \int_0^{\infty} e^{-t_1 s}\left[\int_0^{t_1} \alpha'(x)E_1\,(t_1 - x)dx\right]dt_1 \tag{42}$$

Since $\sigma(t_1)$ is constant, the left side of (42) becomes:

$$\sigma \int_0^{\infty} e^{-t_1 s}\,dt_1 = \frac{\sigma}{s} \tag{43}$$

The right side of expression (42) can be converted to:

$$\int_0^{\infty} e^{-t_1 s} \int_0^{t_1} \alpha'(x)E(t_1 - x)dxdt_1 = f(s)\cdot g(s) \tag{43a}$$

where

$$f(s) = \int_0^{\infty} e^{-t_1 s}\,E(t_1)dt_1 \tag{43b}$$

and

$$g(s) = \int_0^{\infty} e^{-t_1 s}\,\alpha'(t_1)dt_1 \tag{43c}$$

By equating (43) and (43a) there is obtained:

$$\frac{\sigma}{s} = f(s)\cdot g(s) \quad \text{or} \quad f(s) = \frac{\sigma}{s\cdot g(s)} \tag{44}$$

By introducing $\alpha'(t_1)$ from (36) into (43c):

$$g(s) = \int_0^{\infty} e^{-t_1 s}\cdot\frac{\sigma}{b}\cdot\frac{1 - e^{-ct_1}}{t_1}\,dt_1 = \frac{\sigma}{b}\ln\left(1 + \frac{c}{s}\right) \tag{45}$$

Substituting this in (44) then:

$$f(s) = \int_0^{\infty} e^{-t_1 s}\,E(t_1)dt_1 = \frac{b}{s\cdot\ln\left(1 + \frac{c}{s}\right)} \tag{46}$$

Using the formula for the reversion of the Laplace transformation, there is obtained for $E(t_1)$:

$$E(t_1) = \frac{1}{2\pi i}\int_{\beta - i\infty}^{\beta + i\infty} e^{t_1 s}\cdot f(s)ds \tag{47}$$

The integration is to be taken in the complex plane over a parallel to the imaginary axis, where the distance β from the imaginary axis is arbitrary, however, for the function $e^{t/s} \cdot f(s)$ not to have any singularities on its positive side. Integration in the complex plane gives:

$$E(t) = \int_0^c \frac{b}{s \cdot \left\{ \left[\ln \left(\frac{c}{s} - 1 \right) \right]^2 + \pi^2 \right\}} e^{-ts}\, ds \tag{48}$$

Putting $s = 1/\tau$, there is obtained:

$$E(t) = \int_{1/c}^{\infty} \frac{b}{\tau \{ [\ln (c\tau - 1)]^2 + \pi^2 \}} e^{-t/\tau}\, d\tau \tag{49}$$

By comparing this expression with the function introduced earlier, it is seen immediately that (49) agrees with (3) by putting

$$\frac{dE_0}{d\tau} = \frac{b}{\tau} \cdot \frac{1}{[\ln (c\tau - 1)]^2 + \pi^2} \quad \text{for} \quad \tau > \frac{1}{c} \tag{50}$$

and

$$\frac{dE_0}{d\tau} = 0 \qquad \text{for} \quad 0 < \tau < \frac{1}{c} \tag{50a}$$

Equations (50) and (50a) represent the desired function, *i.e.*, the relaxation time spectrum which corresponds to the experimentally determined flow curves (33) or (34).

Discussion of the relaxation time spectrum; approximations

According to (50a), the relaxation time spectrum has a lower limit of $\tau = 1/c$, in that the distribution density, $dE_0/d\tau$, of the elastic modulus for relaxation times which are smaller than $1/c$ disappears according to (50a). For rubber, $c = 10^{35}$/sec (see Table I). The limit beyond which the distribution density of the elastic modulus disappears lies at $t = 10^{-35}$ sec.

The break-off of the spectrum at $\tau = 1/c$ results from the arbitrary way in which the empirical expression (33) has been replaced by the function (34), the latter function remaining finite at $t = 0$. The break-off at $t = 10^{-35}$ sec. does not, therefore, have any physical significance. It can be said generally that the empirical relation (33) permits conclusions only as to the nature of the relaxation time spectrum in the range in which (33) is experimentally defined, namely, for 10^{-2} sec $< t < 10^4$ sec.

The range of the relaxation time spectrum, as far as Equation (50a) is involved, is far removed from the region (10^{-2} sec $< t < 10^6$ sec). This latter region is the one within which use of the equations is justified. It would be unjustifiable to make any statement about the regions defined by (50a) ($t < 10^{-35}$ sec) on the basis of the present observations.

The same is really true also for a large portion of the regions given for (50). For $\tau < 10^{-2}$ sec. and for $\tau > 10^4$, (50) is an extrapolation which possibly is not correct. Equation (50), for relaxation times which are smaller than 10^{-4}, is apparently incorrect, and there exist indications according to which the density of the elastic moduli (for $t < 10^{-4}$ sec) is greater than according to (50).

Since Equations (50) and (50a) include material statements relating to regions lying outside the range covered by the empirical values (33a), it is

essential also in the following to show that the restoring force mechanisms, attributed to rubber according to (50), as far as their relaxation times lie beyond the range (33a), do not play a significant role in the practical behavior of the substance in the range (33a).

For the factor on the right side of (50), the designation $h(\tau)$ is introduced in order to continue the discussion of this relation:

$$h(\tau) = \frac{1}{[\ln (c\tau - 1)]^2 + \pi^2} \tag{51}$$

The relation (50) for the description of relaxation time spectrum, for all practical purposes, then reads:

$$\frac{dE_0}{d\tau} = \frac{b}{\tau} h(\tau) \tag{52}$$

In a soft vulcanized rubber examined by us, c was about 10^7/sec. (see Table I). Consequently for the range (33a) of interest to us, as well as for values of τ in the neighborhood of range (33a)

$$c\tau \gg 1 \tag{53}$$

(51) then becomes

$$h(\tau) = \frac{1}{(\ln c + \ln \tau)^2 + \pi^2} \quad \text{for } c\tau \gg 1 \tag{54}$$

or, considering (35a)

$$h(\tau) = \frac{1}{(a - \epsilon + \ln \tau)^2 + \pi^2} \tag{54a}$$

For the region of interest:

$$|\ln c| \gg |\ln \tau| \quad \text{and } \ln c \gg \pi \tag{53a}$$

so that (54) becomes:

$$h(\tau) = \frac{1}{(a - \epsilon)^2} \quad \text{for } c\tau \gg 1;\ |\ln c| \gg |\ln \tau|;\ \ln c \gg \pi \tag{54b}$$

or, if $\ln \tau$, π^2, and also the value of ϵ are neglected as small quantities compared with a in the denominator of (54a):

$$h(\tau) = \frac{1}{a^2} \quad \text{for } c\tau \gg 1;\ |\ln c| \gg |\ln \tau|;\ \ln c \gg \pi \tag{54c}$$

In the case of practical interest, the relaxation time spectrum (50) thus becomes:

$$\frac{dE_0}{d\tau} = \frac{b}{a^2} \cdot \frac{1}{\tau} \quad \text{for } c\tau \gg 1;\ |\ln c| \gg |\ln \tau|;\ \ln c \gg \pi \tag{55}$$

In the first approximation, the function $dE_0/d\tau$, which describes the distribution density of elastic modulus, is hyperbolic; the distribution density $dE_0/d\tau$, according to (55), is inversely proportional to the value τ in whose environment the distribution density is sought. The proportionality factor, b/a^2, can be evaluated from the rate of change of length, $\Delta l/l$, given by Equation (33), the latter describing the flow as a function of the time t at a known fixed stress σ (see Table I).

In Figures 1a and 1b, the exact course of the relaxation time spectrum (50) is reproduced on natural (1a) as well as double logarithmic scales (1b). In

Figure 1b the approximation (55) is sketched as a dotted line (on the scale of 1a, the two curves fall practically together). For a and b, the values obtained with a pure soft vulcanized rubber were introduced (Table I, last line).

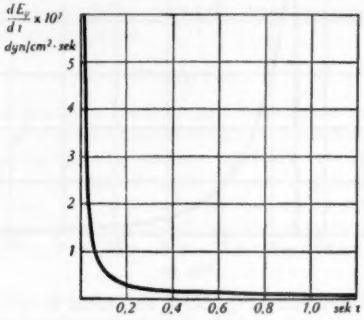


FIG. 1a.

Figure 1a shows the distribution density $dE_0/d\tau$ of the partial elastic modulus as a function of the relaxation time τ for lightly vulcanized pure rubber. The figure is related to the example in the last line of Table I with $b = 10^8$ dynes per sq. cm. and $\ln c = 14.5$. The exact solution (50) and the approximation (55) are not distinguishable in this reproduction.[19]

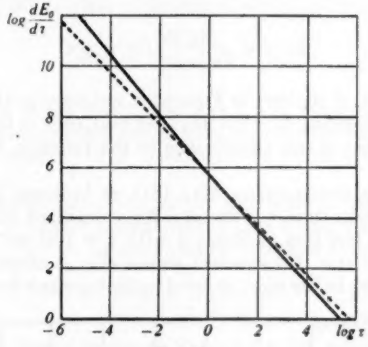


FIG. 1b.

Figure 1b shows the distribution density $dE_0/d\tau$ of the partial elastic modulus as a function of relaxation time τ for the same example as Figure 1a for a somewhat wider range of relaxation times. A double logarithmic scale is used.

Solid curve = exact solution by (50)
Dotted curve = approximation by (55)

Then it is seen that $h(\tau)$ decreases with increasing τ instead of being constant as the approximation (54c) requires, *i.e.*, the $dE_0/d\tau$ according to (52) decreases with increasing τ faster than the proportionality to $1/\tau$.

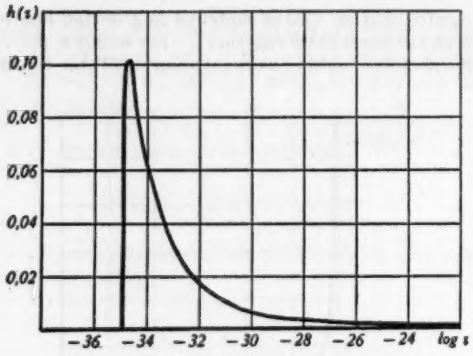


FIG. 2a.

The course of the function $h(\tau)$, which according to (54c) would equal $1/a^2$, is represented in Figures 2a and 2b for the sample of rubber examined by Brenschede. The function $h(\tau)$ is taken as the ordinate and the logarithm of the relaxation time τ as the abscissa. From the figure as well as Equation (57), it can be seen that $h(\tau)$ increases quickly from the lower limit of the spectrum at $\tau = 1/c$ and reaches a maximum at $\tau = 2/c$. For larger values of τ, h decreases approximately hyperbolically plotted against log τ, but so slowly that it has, in the entire interval of practical significance (33a), approximately the value $1/a^2$ (see Figure 1b). For very large τ values, it ultimately approaches the value:

$$h(\tau) = \frac{1}{(\ln \tau)^2} \quad \text{for } \tau \gg c \tag{54d}$$

The function $h(\tau)$ is plotted in Figure 2a, not only in the region (33a), but also beyond it. According to what has been said, only in the range (33a) is one justified in attributing a real significance to the function $h(\tau)$ or the function (52).

Figure 2a shows the function $h(\tau)$ (51) as ordinate plotted against the logarithm of relaxation time τ (τ in sec.) for vulcanized loaded rubber. (Example: The second last line of Table I with $c = 10^{35}$ sec^{-1}.) The curve for $h(\tau)$, valid for other (*e.g.*, for smaller) values of c, is obtained by shifting the curve reproduced here to the right parallel to the log τ axis by an amount 35-log c.

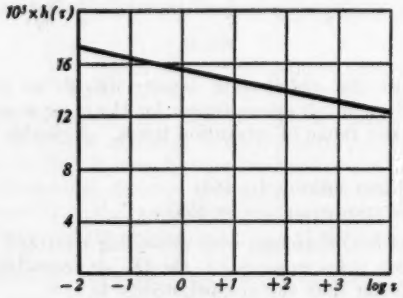


FIG. 2b.

Figure 2b shows the function $h(\tau)$ (ordinate) as a function of the logarithm of relaxation time τ (abscissa) for the same example as Figure 2a; this figure is covering the range of practical importance, *viz.*, $\tau = 10^{-2}$ sec to $\tau = 10^{4}$ sec.

The curves of Figure 2 are true for rubber which has a value of $\log c = 35$. By shifting these curves parallel to the τ axis, the corresponding curves for other substances examined are obtained.

SUMMARY

By rapid deformation of a medium in which linear molecules are present, various changes are produced simultaneously in the latter. These changes are more or less independent of one another, and can release independently and totally or partially by rearrangement of valence distances and valence angles in the chain molecules. By virtue of such relaxation processes, a portion of the stress originating in the rapid deformation disappears, with a changing time requirement for the various portions. A relaxation time spectrum is thus formed.

The relaxation time spectrum consists of a finite number of restoring force mechanisms with proper relaxation times or of a continuous spectrum.

Both the creep curves (the dependence of the length of a body on time at constant load), and stress relaxation (decay of the stress observed in test sample kept at constant length after rapid deformation), as well as the total visco-elastic behavior, especially the behavior at constant periodic deformation of the test sample, are determined by the relaxation time spectrum.

The appropriate quantitative relationships were derived.

In considering a continuous relaxation time spectrum, the E modulus (to be) observed at the time t after producing a rapid deformation is:

$$E(t) = \int_0^\infty \frac{dE_0}{d\tau} e^{-t/\tau}\, d\tau$$

$dE_0/d\tau$ is a function of the relaxation time t, and represents the density with which the partial elastic moduli are distributed over the various portions of the relaxation time spectrum. The determination of this function is the real problem of this work.

Starting from Brenschede's empirical relationship, taken from the creep curve, according to which time dependence of the elastic modulus in a large time interval (about $\tau = 10^{-2}$ to 10^{4} sec.) can be represented by the relation:

$$E'(t) = \frac{b}{a + \ln t}$$

It is possible to find, and to represent by formula, the actual existing relaxation time spectrum for rubber and similar substances.

This relationship is modified in such a way that it remains finite for $t = 0$, and, in the experimentally examined range, is identical with the function given by Brenschede. With the aid of the modified function summarizing the result of flow observations, the essentially mathematical problem to determine the relaxation time spectrum of rubber or related substances from the experimental visco-elastic behavior of these compounds is solved.

The distribution density of the partial elastic-modulus is given approximately by:

$$\frac{dE_0}{d\tau} = \frac{b}{a^2} \cdot \frac{1}{\tau}$$

It is, thus, approximately inversely proportional to the relaxation time τ. The intensity of the relaxation time spectrum thus increases to very high values in the range of small values of τ.

A discussion of the resulting elastic and viscous behavior appears in Part II.

II

In Part I of this series[20], the occurrence of a widespread relaxation time spectrum was established for materials, such as rubber, which are composed of high molecular-weight linear molecules. Relationships were given which described the mechanical and visco-elastic behavior of materials when the relaxation time spectrum was given. On the basis of the creep curve (dependence of the change of length of a test sample on time at constant load) observed for rubber and similar materials, a quantitative expression was given for the density distribution of the elastic moduli in the various regions of the relaxation time spectrum[21].

In this second paper, the distribution density of the observed elastic moduli will be discussed and conclusions drawn regarding the elastic and viscous behavior resulting from it. Particularly in the discussion of the viscous behavior, new facts are brought to light. Moreover, an attempt will be made to construct a model to explain the assertions made about relaxation time spectrum.

The numbering of the sections and formulas follows in sequence from Part I.

DESCRIPTION OF THE ELASTIC-VISCOUS BEHAVIOR ON THE BASIS OF THE RELAXATION TIME SPECTRUM

When the relaxation time spectrum is known according to Equation (50), the elastic and viscous behavior can be thoroughly understood. Conclusions drawn on this basis will, however, only be exact insofar as, in making them, the relaxation time spectrum in the range (33a) has been utilized, *i.e.*, in the range $10^{-2} < \tau < 10^{4}$ sec.

Stress relaxation after rapid deformation

Equation (49) is obtained by substituting (50) in (3); (49) representing the elastic modulus, $E(t)$ (Equation 3), as a function of the time t, a magnitude which can be determined experimentally by measuring the restoring force at the time t after rapid deformation.

The exact function $E(t)$ resulting from this expression can be obtained by integrating (49) graphically (with respect to τ) for the desired values of t.

Moreover, the evaluation has practical interest only in the region (33a), *i.e.*, for relatively large values of t. In this case, some simplifications of the relevant equations are possible. Such an approximation can be obtained by replacing the factor $e^{-t/\tau}$ appearing in (49) by a value $f(t, \tau)$ where:

$$f(t, \tau) = 0 \text{ for } \frac{t}{\tau} > 1 \text{ or for } t > \tau$$

$$1 \text{ for } \frac{t}{\tau} < 1 \text{ or for } t < \tau \qquad (56)$$

Since the denominator of (49) does not change greatly in the region where the value of $e^{-t/\tau}$ goes from 0 to 1, and since the contribution to the integral

coming from this range is small in comparison with the absolute magnitude of the entire integral, the error committed by introducing the approximation (56) is not of great importance.

The integration of (49) can now be carried out easily. When the time t, for which the value of E according to (49), is greater than $1/c$, then $1/t < c$; the integral (49) becomes in this case, considering (56):

$$E(t) = \int_{1/c}^{\infty} \frac{b \cdot e^{-t/\tau}\, d\tau}{\tau\{[\ln (c\tau - 1)]^2 + \pi^2\}} \cong b \int_{t}^{\infty} \frac{1 \cdot d\tau}{\tau\{[\ln (c\tau - 1)]^2 + \pi^2\}}$$

$$= b \int_{\ln t}^{\infty} \frac{d \ln \tau}{[\ln (c\tau - 1)]^2 + \pi^2} \cong b \int_{\ln t}^{\infty} \frac{d \ln \tau}{(\ln c + \ln \tau)^2}$$

$$= \frac{b}{\ln c + \ln t} \quad \text{(approximation)} \qquad (57)$$

If we put $\ln c \cong a$ on the basis of (35a) and (35b), then this becomes:

$$E(t) = \frac{b}{a + \ln t} \quad \text{or} \quad \frac{1}{E(t)} = \frac{a + \ln t}{b} \quad \text{(approximation)} \qquad (58)$$

Comparison of the elastic moduli E and E′ determined, respectively, from the stress relaxation and from the creep curve

The right side of Equation (58) corresponds to the right side of Brenschede's empirically found relationship (33), on the basis of which the relaxation time spectrum has been calculated. But the left side of (58), *i.e.*, $E(t)$, differs in value from the left side of Equation (33), *i.e.*, from $E'(t)$. The comparison of (58) and (33) shows that the two previously differing values of $E(t)$ according to Equation (2) and $E'(t)$ according to Equation (32) becomes equivalent to one another in the approximation considered here. In other words, the course of

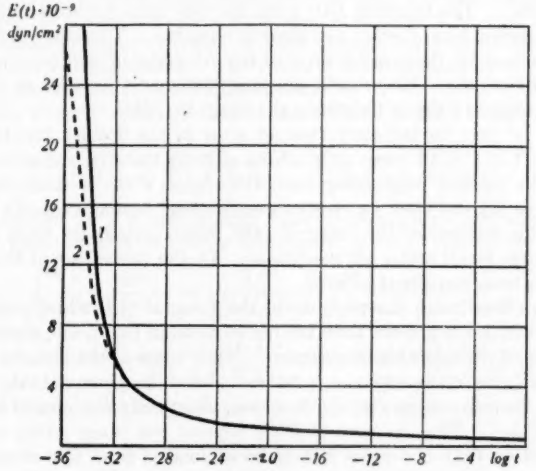


FIG. 3.

the reciprocal value of the stress σ within a definite time, which is observed following a rapid deformation to a constant value, corresponds to the course of the relative change of length within the same definite time, which is observed after rapidly applying a stress and then holding the stress constant, or still more simply, the elastic moduli, which are calculated from the stress relaxation (Equation 3) and from the creep curve (Equation 32), correspond approximately, the correspondence including the value and the dependence on time.

Actually the degree of correspondence is extensive. This is illustrated in Figure 3. Curve 1 represents E' for rubber calculated according to Equation (33), using the values of a and b given in Table I (4th line). The value $E(t)$ calculated from the exact Equation (49) is given by curve 2 (dotted). The two curves cannot be distinguished in the region 10^{-2} sec. $< t < 10^{4}$ sec., that is, in the region in which the formulas claim to represent the actual behavior of the material. A noticeable difference between the two curves occurs first outside the range of practical interest (33a), beyond $t = 10^{24}$ sec.

Figure 3 showing the dependence of the elastic modulus on time for vulcanized loaded rubber (second last line of Table I). In this figure, the solid curve is an approximation according to Equation (33), and the broken curve is an exact solution according to Equation (49).

The E modulus at the instantaneous time t as a function of the sum of all parts of the relaxation time spectrum

Influence of error in the representation of the relaxation time spectrum on the value of E calculated at time t.

According to (49), the E modulus at time t is considered as a sum made up of contributions from all parts ($\tau = 0$ to $\tau = \infty$) of the relaxation time spectrum. From what has been said, it can be expected that the relaxation time spectrum (dependence of the integrand in (49) to τ) is adequate for τ values which correspond to the region (33a), but is not so good for τ values which lie beyond (33a). The function $E(t)$ given by (49) thus contains some contributions, the correctness of which are open to question. Therefore, it is justifiable to question how far the possible error of the integrand of (49) for τ values which lie beyond the range (33a) might practically distort the value of the function $E(t)$ for values of t which lie within the range of (33a).

It can be seen immediately that an error in the density function lying in region $\tau < t$ or $\tau < 10^{-2}$ sec. only affects slightly the $E(t)$ values of the region (33a). The portion originating from the region $\tau < t$ is multiplied by $e^{-t/\tau}$ according to (3) and (49), *i.e.*, with a number that becomes rapidly small when $t > \tau$. This portion of the integral (49), which originates from the regions $\tau < t$, is thus small under all conditions. In the derivation of Equation (58) it has even been put equal to zero.

On the other hand, the portions of the integral (49) which originate from regions in which τ is greater than the limits given in (33a), *i.e.*, greater than 10^{4} sec., can be of considerable importance. That value of the integral (49) which results if $dE_0/d\tau$ in the region $\tau > 10^{4}$ sec. should be given actually by a function other than Equation (50), is, however, practically unchanged in the entire range of (33a). That is, even if $E'(t)$ beyond the range (33a) is no longer represented by (33), the value $E(t)$ to be calculated from (50) remains correct in the region of (33a) except for an additive constant.

Elastic modulus for periodic displacement

The elastic modulus $E(t)$, determined from the restoring force present at the time value t after rapid deformation, was given by (49) or approximately by (58). It is, thus, a function of time t. As has already been shown, a material whose relaxation time spectrum is known can be associated with a specific elastic modulus independent of the time provided the test-sample is periodically displaced (Equation 23). The elastic modulus then depends basically on the angular velocity ω, which is used in the periodic displacement (Equation 28). When the relaxation time spectrum is given by (50), the elastic modulus characteristic for the periodic displacement is obtained by introducing this value of $dE_0/d\tau$ into (28):

$$E(\omega) = \frac{b}{\ln c - \ln \omega} \quad \text{for} \quad (\ln c - \ln \omega) \gg 1 \tag{59}$$

When the time period ($T_s = 2\pi/\omega$) of the periodic displacement under consideration is in the region (33a) (the region between 10^{-2} and 10^4 sec.), then for most types of rubber listed in Table I, $|\ln c| \gg \ln \omega$. In this case (59) becomes:

$$E(\omega) \cong \frac{b}{a} \quad \text{for} \quad |\ln c| \gg |\ln \omega| \tag{59a}$$

This means that the dynamic elastic modulus in the region (33a) is practically independent of the frequency. This further signifies that the intensity of the distribution function in this region (the region 33a) is so small that the restoring force mechanisms, whose relaxation times fall in the region (33a), contribute to an unimportant extent to the practical elastic behavior (dynamic elastic modulus).

Circumstances in the case of viscosity are different in this respect.

Viscosity

It has been shown that it is not possible by ordinary means to assign a viscosity to a material whose relaxation time spectrum extends to $\tau = \infty$. However, a definition of viscosity is still possible in this case if the material is subjected to periodic displacement. The viscosity then depends on the frequency ω of the periodic displacement (Equation 22).

When $dE_0/d\tau$ from (50) and (50a) is substituted in (22), there is obtained:

$$\eta = \frac{1}{2(1+\mu)} \int_{1/e}^{\infty} \frac{b}{\tau} \frac{1}{[\ln (c\tau - 1)]^2 + \pi^2} \cdot \frac{\tau \cdot d\tau}{\omega^2\tau^2 + 1} \tag{60}$$

The expression for η is particularly clear when the approximation (55) instead of the exact expression (50) is substituted in (22). This gives:

$$\eta = \frac{1}{2(1+\mu)} \int_0^{\infty} \frac{b}{a^2} \cdot \frac{d\tau}{\omega^2\tau^2 + 1} = \frac{1}{2(1+\mu)} \cdot \frac{b}{a^2} \int_0^{\infty} \frac{1}{\omega} \cdot \frac{dz}{z^2 + 1}$$

$$= \frac{1}{2(1+\mu)} \frac{b}{a^2} \frac{1}{\omega} [\arctan z]_0^{\infty} = \frac{1}{2(1+\mu)} \cdot \frac{b}{a^2} \cdot \frac{\pi}{2\omega} \tag{61}$$

In this evaluation the integration variable z is set equal to $\omega\tau$. Thus, when:

$$\frac{2\pi}{\omega} = T_s \tag{62}$$

is the period in seconds, then:

$$\eta = \frac{1}{2(1+\mu)} \cdot \frac{b}{a^2} \cdot \frac{T_s}{4} \tag{63}$$

When the material is periodically deformed, the viscosity is thus directly proportional to the period T_s at which the experiment is performed. This relationship is true for all materials whose creep curves are given by Equation (33).

When the numerical values of a and b from Table I, 4th line, are substituted and the Poisson ratio is set: $\mu = 0.5$ and $T_s = 10$ sec., then:

$$\eta = \frac{4.0 \cdot 10^9}{80^2 \cdot 3} \cdot \frac{10}{4} = 5.2 \times 10^5 \text{ poises} \quad (T_s = 10 \text{ sec.}) \tag{63a}$$

becomes the viscosity of the loaded rubber examined by Brenschede. For the pure rubber examined by us (Table I, last line), similarly:

$$\eta = 3.7 \times 10^5 \text{ poises} \quad (T_s = 10 \text{ sec.}) \tag{63b}$$

and for Buna (Table I):

$$\eta = (3 - 5) \times 10^6 \text{ poises} \quad (T_s = 10 \text{ sec.}) \tag{63c}$$

Van der Wyk[22] has found a viscosity of several million poises by measuring the damping of a mechanical deformation produced in rubber at no precisely given frequency. This agrees with the results found above.

Equation (63) shows that a statement of any exact value of the viscosity for rubber is meaningless as long as the period T_s which is used for the measurements is not stated. According to (63), the viscosity of a material is greater, the larger the period T_s. Thus it is greater, the slower the deformation. The shorter the period, the smaller becomes the opposing viscous resistance to deformation of rubber (whereas the elastic modulus increases somewhat with increasing frequency).

If the viscosity were not dependent on the frequency, the mechanical energy consumed in heat per cc. per second during a periodic shear deformation (15) would be given by (20), and thus be proportional to ω^2. As seen above, for rubber and rubberlike materials, the η value dependent on ω according to (61) must be substituted in (20) instead of a value independent of frequency. When this is done, heat generation per cc. per second is given by:

$$\frac{dA}{dt} = \frac{\omega\pi}{2(1+\mu) \cdot 4} \cdot \frac{b}{a^2} \cdot \gamma_0^2 \tag{64}$$

This generation of heat no longer increases in proportion to ω^2, but only in proportion to ω.

The viscosity decreases with increasing angular velocity ω (Equation 61). The amount of heat generated per unit time, however, is only proportional to ω according to (64), and not proportional to the square as would follow from (20) if η were independent of ω.

Since the Poisson ratio for rubber is close to 0.5, when this is substituted in (64), there is obtained

$$\frac{dA}{dt} = \frac{\pi}{24} \cdot \frac{b}{a^2} \gamma_0^2 \omega \tag{64a}$$

for the heat generated per cc. in a piece of rubber which has been deformed by shear with an angular velocity $\omega(\omega/2\pi$ cycles per second) and with an amplitude γ_0.

When the experimental material is deformed periodically by elongating and(or) compressing instead of by shear, the heat generated per cc. is given by:

$$\frac{dA}{dt} = \frac{\pi}{8} \cdot \frac{b}{a^2} \alpha_0^2 \omega \tag{64b}$$

in which the relative change in length $\Delta l/l = \alpha_0 \sin(\omega t)$ in a piece of rubber which has been deformed by elongation or compression with an angular velocity ω and with an amplitude α_0.

Equations (64b and a) can be of theoretical interest, and certainly are of practical interest, for they give the energy consumed in heat per cc. in the experimental material as a function of the frequency and amplitude of the imposed deformation. The proportionality factor b/a^2 in (64a) and (64b) can, moreover, be determined simply, in that a and b are determined from the creep curve of the experimental material, *i.e.*, from the time dependence of the observed deformation with constant load according to Equation (33) (Table I).

Equation (63) has been confirmed by the experiments described in another paper[23].

For a more exact study, and especially in going to experiments with high angular velocities ω, approximations (61) and (63) no longer suffice. Therefore, Equation (60) must be used in order to evaluate it more exactly than can be done with (61) (and following). Notice at once that, by replacing the expression $[\ln(c\tau - 1)]^2 + \pi^2$ by a^2, which converts (60) into (61), the denominator of (60) is generally reduced below the actual value, so that too large a viscosity η results using (61).

In order to find a better approximation, substitute in (60):

$$\ln \omega\tau = x; \quad \tau = \frac{e^x}{\omega} \tag{65}$$

Which then becomes:

$$\eta = \frac{b}{2(1+\mu)} \int_{\ln \omega/c}^{\infty} \frac{e^x}{\omega} \cdot \frac{1}{\left[\ln\left(c\frac{e^x}{\omega} - 1\right)\right]^2 + \pi^2} \frac{dx}{e^{2x} + 1} \tag{66}$$

Since it has been assumed that $c/\omega \gg 1$, this becomes:

$$\eta = \frac{b}{2(1+\mu)} \frac{1}{\omega} \int_{\ln \omega/c}^{\infty} \frac{1}{\left(\ln\frac{c}{\omega} + x\right)^2 + \pi^2} \cdot \frac{dx}{2 \operatorname{Cos} x} \tag{66a}$$

When $\omega \ll c$, the lower limit is $\ln \omega/c \ll 0$. The factor $1/\operatorname{Cos} x$ decreases for $x > 0$ as well as for $x < 0$, approximately as e^{-x}. In the region in which $1/\operatorname{Cos} x$ is not very small, *i.e.*, in the region $-2 < x < +2$, the expression $(\ln c - \ln \omega + x)^2 + \pi^2$ in (66a) changes so little that it becomes approximately constant and equal to the value which it assumes for $x = 0$. It then becomes:

$$\eta = \frac{b}{2(1+\mu)} \frac{1}{\omega} \frac{1}{(\ln c - \ln \omega)^2 + \pi^2} \int_{\ln \omega/c}^{\infty} \frac{dx}{2 \operatorname{Cos} x}$$

$$= \frac{b}{2(1+\mu)} \frac{1}{\omega} \frac{1}{(\ln c - \ln \omega)^2 + \pi^2} [\operatorname{arc\,tg} e^x]_{\ln \omega/c}^{\infty} \tag{66b}$$

When $\omega \ll c$, the lower limit of the integral on the right side can be considered as 0. There is then obtained:

$$\eta = \frac{b}{2(1+\mu)} \cdot \frac{\pi}{2\omega} \cdot \frac{1}{(\ln c - \ln \omega)^2 + \pi^2} \tag{66c}$$

The last factor on the right side of (66c), as shown by a comparison with (54), equals:

$$h\left(\frac{1}{\omega}\right) = \frac{1}{(\ln c - \ln \omega)^2 + \pi^2} = h\left(\frac{T_s}{2\pi}\right) \tag{67}$$

so that in place of (66c) there can be written:

$$\eta = \frac{b}{2(1+\mu)} \frac{T_s}{4} h\left(\frac{T_s}{2\pi}\right) \tag{68}$$

The value of the factor $h(T_s/2\pi)$ as a function of $T_s/2\pi$ can be taken from Figure 2.

In the approximation given by (54c), $h(T_s/2\pi)$ passes over into $1/a^2$ and thereby Equation (68) reduces to Equation (63).

The viscosity for the deformation frequency ω (angular velocity) as a function of all parts of the relaxation time spectrum; the influence of error in representing the relaxation time spectrum on the viscosity for periodic processes whose period T_s corresponds to the interval (33a)

The viscosity of a material deformed with an angular velocity ω (or period $T_s = 2\pi/\omega$) is a sum, according to Equation (22), to which all parts of the relaxation time spectrum contribute.

Therefore, it is of interest to ask how large the relative contribution of the various parts of the relaxation time spectrum becomes in the viscosity computed by (66c) and (63). Since this is a qualitative determination, take as a basis the approximation (61).

Contributions from the region $\tau > T_s$.—It is seen at once that the regions in which $\omega\tau \gg 1$ or, on the basis of (62), $\tau \gg T_s$, do not appreciably contribute to the viscosity. Thus the restoring force mechanisms, whose relaxation times τ are greater than the time used for the periodic deformation of the test-sample, do not appreciably contribute to viscosity. All these mechanisms contribute essentially to the elasticity, as seen in Equation (28). Thus, when the actual distribution function in the region $\tau \gg T_s$ deviates from the distribution calculated by (50) and extrapolated in some cases, the viscosity calculated by Equation (60) or Equation (61) is not greatly affected.

Contributions from the region $\tau < T_s$.—In the region where $\omega\tau \ll 1$ or $\tau \ll T_s$, $\omega^2\tau^2 + 1$ very soon equals approximately 1. Then:

$$\eta = \frac{1}{2(1+\mu)} \frac{b}{a^2} \int_0^{\tau_m} d\tau \tag{69}$$

wherein the upper limit τ_m has to be put approximately equal to $\pi/(2\omega) = T_s/4$ according to (63).

Equation (69) allows the following simple statement to be made. In the region where $\tau \ll T_s$, restoring force mechanisms, whose relaxation time lies between τ and $\tau + d\tau$ give to the viscosity $\eta(T_s)$, a contribution proportional to $d\tau$. The contribution of the interval, $d\tau$, is independent of the part of the

range, $\tau < T_s$, in which the interval, $d\tau$, is selected. Equally wide intervals, $d\tau$, of the spectrum cause equally large contributions to the viscosity.

For example, it follows from this that, for a forced vibration occurring with a period of 10 seconds, about 90 per cent of the friction observed results from the restoring force mechanisms whose relaxation time lies between 1 and 10 seconds, while only 1 per cent results from the relaxation interval $0\text{–}10^{-1}$ second. Generally the principal portion of the viscosity observed in a forced vibration of period T_s results from the restoring force mechanisms whose relaxation time τ is somewhat, but relatively little, smaller than T_s. These conditions are quite the reverse of those discussed in the case of dynamic elastic modulus, for there it was established that the restoring force mechanisms, whose relaxation times lie in the region T_s or are smaller than T_s, contribute practically nothing to $E(T_s)$. (See Equation 59a.)

According to (69), the contribution to viscosity made by all the restoring force mechanisms whose relaxation time is shorter than $T_s \times 10^{-3}$ or shorter than $T_s \times 10^{-6}$, respectively, represents only about one thousandth and one millionth part, respectively, of the total viscosity observed in a forced vibration of period, T_s. This contention is true when $dE_0/d\tau$ is actually given by (50). But it is also practically true when $dE_0/d\tau$ in the range $\tau \ll T_s$ deviates more or less from (50).

Deviations of the actual distribution function (50) in the region $\tau \ll T_s$ when the deviations are not very large are, indeed, scarcely noticeable in the viscosity. The limited influence of such deviations, as far as such an influence appears at all, is a small constant which has to be added to the viscosity calculated by (60) and which has the same value throughout the entire range (33a).

Phase displacement between deformation and stress; phase angle

When the expressions for viscosity and elastic modulus, (66c) and (59), are substituted into (31), there is obtained for phase displacement between deformation and stress:

$$\tan \varphi = \frac{\pi}{2\omega} \cdot \frac{\ln c - \ln \omega}{(\ln c - \ln \omega)^2 + \pi^2} \tag{70}$$

or, when $(\ln c - \ln \omega) \gg \pi$:

$$\tan \varphi = -\frac{\pi}{2\omega} \cdot \frac{1}{\ln c - \ln \omega} \tag{70a}$$

Using the approximations (59a) and (63), there is obtained:

$$\tan \varphi = -\frac{T_s}{4a} \qquad \text{(70b) (approximation)}$$

STATEMENTS REGARDING RELAXATION TIME SPECTRUM IN THE REGION OF VERY LARGE AND VERY SMALL τ VALUES

It has been emphasized repeatedly that an accurate statement about relaxation time spectrum can be made only in the range of (33a) (for 10^{-2} sec. $< \tau <$ 10^4 sec.) and that statements on the course of the function $dE_0/d\tau$ made, *e.g.*, according to (50) are extrapolations for any region beyond this limit. Certain concrete statements can now be made as to how the actual distribution function $dE_0/d\tau$ in the region beyond the limits of (33a) is likely to differ from the course extrapolated according to (50).

Region of very large τ values

Deviations occurring in the region of large τ values will make their appearance in the behavior of the elastic modulus, as seen in Equation (49). If (49) were extremely accurate, Equations (57) and (58) would be true in the regions of large t values; that is, $E_0(t)$ would equal 0 when $t = \infty$. This is probably not true, but since $E(t)$ decreases slowly with increasing t according to (58), accurate observations must be made to very large values of t in order to establish a real deviation. It is, however, quite probable that $dE_0/d\tau$ decreases less than according to (50) with very large values of τ, and in such a way that, by substituting $t = \infty$ in (3), a finite elastic modulus remains.

Region of small τ values

Deviations from (50) in the region of small τ values do not affect the elastic modulus, and only slightly the viscosity. Nevertheless, it can be said positively that (50) is no longer true for very small τ values. This is based on Equation (4a), which is only an order of magnitude determination but, nevertheless, a reliable one. It has nothing to do with the analysis of the spectrum. Statement (4a) can be supplemented from actual experience in that the relaxation time spectrum extends to about 10^{-13} second for low-molecular liquids, for which $\eta = \frac{1}{3} E_0\tau$, about 10^{-2} poise, if E_0 is about 10^{10}–10^{12} dynes per sq. cm. For high-molecular materials, though their relaxation time spectrum differs greatly in some respects from that of low-molecular liquids, it can be expected that at least the lower limit of the relaxation time spectrum is no lower than that for low-molecular liquids. While it is reasonable that some of the relaxation times in high molecular materials are large, there is no reason why any part of the relaxation times should be smaller than for low-molecular materials. For high-molecular and low-molecular materials, the lower limit of the integral in (49) can be put at approximately 10^{-13} second. Thus there is obtained:

$$\int_{10^{-13}}^{\infty} \frac{dE_0}{d\tau}\, d\tau = E_0 = 10^{10}\text{–}10^{12} \text{ dynes per sq. cm.} \tag{71}$$

When, on the other hand, the integral (71) for rubber is formed on the assumption that (50) is true down to $\tau = 10^{-13}$ second (which would be conceivable on the basis of the c values in Table I), there is obtained:

$$\frac{d\tau}{[\ln (c\tau - 1)]^2 + \pi^2} \cong \int_{10^{-13}}^{\infty} \frac{b}{\tau} \frac{d\tau}{(\ln c + \ln \tau)^2} = -\, b \left[\frac{1}{\ln c + \ln \tau} \right]_{-13\times 2.3}^{\infty}$$

$$= \frac{4 \cdot 10^9}{80 - 30} \cong 10^8 \text{ dynes per sq. cm.} \tag{72}$$

This is a value which is at least two decades below the value of (71). The difference lies beyond the limit of error due to experimental error and inaccuracy of the approximation. Therefore, it is to be assumed that (50) and, accordingly, also Equation (33) in the region $10^{-13} < \tau < 10^{-2}$ second is inaccurate, and in such a way that $dE_0/d\tau$ increases more than function (50) in the region of smaller relaxation times. The last statement is confirmed by experimental determinations carried out by ourselves in that the creep curve of rubber in the region of smaller times deviates from the course of (33) in the direction of somewhat larger E' values.

SIGNIFICANCE OF RELAXATION TIME SPECTRUM

In order to find the relaxation time spectrum, only the assumption of the existence of a spectrum as well as the empirical relationship (33) was necessary. No assumptions were necessary about the ways and means of how the spectrum forms. Inversely, it is not possible, without producing additional arguments, to use Equation (50) for any model construction. Certain conclusions offer themselves meanwhile for rubber and rubberlike materials based on the kinetic theory of rubber elasticity[24], at least for part of the relaxation time spectrum.

Kinetic origin of restoring forces possessing large and moderate relaxation times

In soft vulcanized rubber, the restoring force mechanism whose $\tau_1 = \infty$ and whose E_{10} equals about 10^5–10^6 dynes per sq. cm., comes from the circumstances that the molecular filaments whose end points are the vulcanization sites (the cross-linking points) are partially oriented and partially uncoiled when the test-sample is stretched. For this mechanism:

$$E_{10} = 7\frac{RT\rho}{M_f'} \tag{73}$$

where M_f' is the average molecular weight of the linear portions designated as the lattice links lying each between two vulcanization sites, and ρ is the density. When the fact is taken into account that the possible shape of a given lattice link is not only limited by the chemical vulcanization points fixing the ends of the link, but also partially by the steric effects produced by foreign vulcanization sites[25] present in the sample, E_{10}, becomes (in place of 73):

$$E_{10} - 3\frac{RT\rho}{M_f} \tag{74}$$

where M_f is the molecular weight of a lattice link evaluated by taking account of both chemical and physical vulcanization points.

For soft vulcanized rubber, the restoring force mechanism, which is related to the large relaxation times, thus comes from the orientation and configuration of the lattice links. Here, at least in the case of moderate degrees of stretching, a force due to a pure probability mechanism is acting.

For rubber and rubberlike materials, however, not only may the restoring force mechanisms for which $\tau = \infty$ be due to the probability mechanism, but also all mechanisms for which τ is greater than about 10^{-2} second.

Several statements mentioned in the introduction can be cited to support the previous statement. When a statistically large coiled linear molecule[26] is deformed, together with the mass embedding it, not only will the linear coil as a whole be distorted, but also the smaller parts of the linear coil will be moved with respect to one another. As indicated previously, these small parts of the linear molecule return to a normal state quickly by Brownian movement after deformation in the embedding mass, because it is necessary to move them only a short distance for this, whereas larger linear sections or the molecule itself require more time. Thus the occurrence of relaxation time spectrum has been correlated with the return of the molecule or the linear parts of it to the normal state, because by this the corresponding stresses disappear.

The restoring force fraction corresponding to an energy storing mechanism, *i.e.*, to distorted valence angles and atomic distances, disappears most rapidly because the atoms or atomic groups concerned need to travel only a short dis-

tance to return to the normal state after being distorted, whereas each probability mechanism, *i.e.*, each change of the configuration of a lattice link requires much more time.

Consider now a section of a lattice link, a piece of molecular weight M^*; its configuration will be changed by a rapid deformation of the test-sample and the chain section will consequently keep its altered configuration for a time t^* (which increases with M^*). If the restoring force is measured at time t^* after deformation, the linear sections of molecular weight M^* contained in the material behave as if they had been prevented from returning to their normal state by the action of physical or chemical vulcanization bonds. Linear sections of a molecular weight notably smaller than M^* would, however, have returned to their normal shape again at the time point t^*. When the E modulus is determined it should now be designated as E^*, at time t^* after deformation, by analogy to (74):

$$E^*(t^*) = 3\frac{RT\rho}{M^*} \tag{75}$$

M^* is then, as previously shown, the molecular weight of the linear sections, which require approximately a time t^* or greater in order to change noticeably their configuration by Brownian movement in the elastic embedding medium. According to this concept, the E modulus E^* decreases with increasing time t^*, because the molecular weight M^*, which requires time t^* to change its configuration, increases with increasing time. This dependence will be referred to later.

Before this is done, some considerations concerning the possible value of M^* will be added and references made to some experimental data.

Comparison of possible M^* values for vulcanized and unvulcanized samples; bouncing elasticity of the latter

From what has been said, it is clear that M^*, as a small portion of the linear molecule, must necessarily be smaller than the total molecular weight of the molecule or of the lattice link. When t^* is made sufficiently small, it is apparent that the M^* (small) pertaining to t^* should, for vulcanized and unvulcanized samples of the same material, have approximately the same size. This would mean, according to (75), that $E^*(t^*)$ in regions of sufficiently small values of t^* may follow similar relationships for vulcanized and unvulcanized samples. Differences must then appear when M^*, with increasing time t^*, becomes approximately equal to the true molecular weight M of the linear molecule in the case of unvulcanized materials, or equal to the lattice link weight M_f in the case of vulcanized material.

When M^* in unvulcanized materials has become equal to the true molecular weight M of the molecule, then at a time t pertaining to the molecular weight M, all changes in configuration, which have been imposed by rapid deformation of the sample at the time point $t = 0$, have disappeared and the elastic modulus E^* has, consequently, become 0 after this time.

Thus for unvulcanized material, any arbitrary value of the elastic modulus can be found by suitably choosing the time point t. For unvulcanized homogeneous polymeric materials, a dependence on the degree of polymerization can, however, be expected, such that the maximum time t, after sudden deformation at which a noticeable elastic modulus still can be determined, is about equal

to the time of change of configuration of a molecule of molecular weight M, this time t increasing with M. Thus, for unvulcanized materials, the time after deformation within which the restoring force must be determined in order that a measurable force can be found is shorter, the smaller the degree of polymerization. This agrees with the behavior observed in polymeric unvulcanized materials and has been previously reported[27].

This low-molecular Buna is a viscous mass without the elasticity of rubber. With increasing polymerization, a mass is obtained which flows very slowly, *e.g.*, over a period of a day, and which can be made into any shape by light constant pressure. But this material reacts like rubber when it is rapidly deformed (so called bounding elasticity).

If the degree of polymerization is increased still more, products are obtained which are completely reversibly elastic at short elongations, but which flow gradually during long and high extensions.

The fact that vulcanized and unvulcanized samples of a high polymer in the region of very small observation times show a quite similar behavior with respect to stress relaxation, speaks well for the concepts used in Equation (75), according to which in both cases a similar mechanism prevails, namely, that for each molecular weight M^* of a chain part, smaller than the total molecule or smaller than the lattice link, there is a relaxation time t^*. The conclusion that these rapidly decaying stresses are due to probability mechanisms cannot, however, be drawn immediately from this analogous behavior of vulcanized and unvulcanized preparations.

Significance of the ratio of birefringence to stress for proof of the presence of probability or energy mechanisms of elasticity

The conclusion mentioned above can be obtained from a discussion of the birefringence established during deformation. For vulcanized rubber, the ratio of deformation birefringence and stress does not depend on the degree of vulcanization; the ratio has the same value for unvulcanized rubber as for vulcanized rubber[28]. The latter statement involves the fact that deformation birefringence and stress for unvulcanized rubber decay according to the same time law. The constancy of the ratio of birefringence and stress had been established in Rossi's experiments during time intervals which were not precisely described. Later the relaxation of birefringence was measured in the time interval 10^{-2} to 1 second[29]. The curve with respect to birefringence is approximately the same as that for the relaxation of the elastic modulus; the proportionality in this region has, however, not been proven with any great accuracy.

An accurate proof of the constancy or inconstancy of the quotients from birefringence and restoring force for very small times may make it possible to decide experimentally at what value of τ pure probability mechanisms or some combination of probability and energy mechanism of the restoring force exist. But from what has been said, it can be safely assumed that, for $\tau = \infty$ to τ values of about 10^{-2} second, probability mechanisms are essentially acting in rubber.

Now when in vulcanized rubber the birefringence as well as the restoring force are due to an orientation and change of length of the lattice link, and if the ratio of these two effects for unvulcanized materials has the same numerical value characteristic for the probability origin of the effects, it follows that the time-dependent restoring force in unvulcanized rubber must also (in the time

interval under consideration) be nothing else than a probability mechanism. The same applies to the corresponding time-dependent portion of the restoring force in vulcanized rubber, and thus to the restoring force mechanisms corresponding to the large and moderate τ values of the relaxation time spectrum.

The time t necessary for complete change of configuration by the linear sections of molecular weight M^*. Dependence of the viscosity η^* of the embedding medium on the molecular weight M^* of the linear sections moving in that medium

From the preceding discussions, and within known limits, the time dependence of the elastic modulus according to (75) can justifiably be correlated with the change in configuration time t^*, which is associated with a linear section of molecular weight M^*. Thus:

$$M_f^*(t) = \frac{3RT\rho}{E^*(t)} \tag{76}$$

The change of configuration time t^* depends in turn on the diffusion constant D^* and this on the viscosity η^* with which the embedding medium counteracts the Brownian movement of the linear sections of molecular weight M_f^*. It would be incorrect to regard η^* as independent of M_f^*, for experiments on diffusion of foreign molecules in elastic bulk rubber have shown that η^* increases very rapidly[30] with M_f^*. Conversely, Equation (76) can be used to derive the dependence of the magnitude of η^* on M_f^* from the empirical behavior of (33) and (58).

Consider the following. A linear section of molecular weight M^* consists of

$$Z = M_f^*/M_g \tag{77}$$

monomeric residues when M_g equals the molecular weight of the polymerized monomer unit[31]. If s_m is the number of monomeric residues contained in a preferential statistical chain element, and A_m the length of the preferential statistical element, the linear section of molecular weight M_f^* consists of:

$$\frac{M_f^*}{M_g} \cdot \frac{1}{s_m} = N_m^* \tag{78}$$

preferential elements. The average square distance, h^{*2}, between the beginning and end points of the linear section under consideration is then:

$$h^{*2} = N_m^* \cdot A_m^2; \quad h^* = \sqrt{N_m^*} \cdot A_m \tag{79}$$

For estimating the hydrodynamic resistance which occurs during movement of the end point of the linear section under consideration in a medium of viscosity η^*, consider that $\frac{1}{2}$ of the linear section, *i.e.*, a chain segment of molecular weight $M_f^*/2$, is localized in the end point. Consideration is here taken of the fact that the translation of the end point of a linear section of molecular weight M_f^* involves the translation of molecular parts belonging to the section of weight M_f^*, as well as a translation of some further elements of the chain, being chemically linked to the "end points" of section M_f^*. Then the force necessary to move each end point of the linear section of molecular weight M_f^* relative to its surroundings with a velocity u is approximately equal to[32]:

$$K = \frac{N_m^* \cdot A_m}{2} \cdot \frac{3\pi}{2} \cdot u \cdot \eta^* \tag{80}$$

The velocity which the linear end point reaches by the action of a force of 1 dyne becomes:

$$\mu = \frac{4}{3\pi} \cdot \frac{1}{N_m^* \cdot A_m} \cdot \frac{1}{\eta^*} \tag{81}$$

The diffusion constant D^* of the linear end point is obtained by multiplying by kT, thus:

$$D^* = \frac{4kT}{3\pi} \cdot \frac{1}{\eta^*} \cdot \frac{1}{N_m^* \cdot A_m} \tag{82}$$

The time t' which the linear end point needs to travel a distance x by diffusion becomes on the basis of (82):

$$t' = \frac{x^2}{2D^*} = \frac{3\pi}{8kT} \cdot \eta^* N_m^* A_m \cdot x^2 \tag{83}$$

Taking into consideration that both end points move, the time which the linear section of molecular weight M^* needs to alter completely its configuration by Brownian movement is obtained when x is substituted in (82) by $h^*/3$ and h^* introduced from (79). This time this becomes:

$$t = \frac{\pi}{24kT} \eta^* N_m^{*2} A_m^3 \tag{84}$$

When N_m^* is substituted on the basis of (78) by M_f^* or on the basis of (79) by h^*, then:

$$t = \frac{\pi}{24kT} \eta^* \frac{M_f^{*2}}{M_g^2 \cdot s_m^2} \cdot A_m^3 \tag{85}$$

or:

$$t = \frac{\pi}{24kT} \eta^* \frac{h^{*4}}{A_m} \tag{86}$$

If the expression in (58) for $1/g^*(t)$ is substituted in Equation (76) there is obtained:

$$M_f^*(t) = 3RT\rho \cdot \frac{a + \ln t}{b} \tag{87}$$

Substituting t from (86) in this equation:

$$M_f^* = \frac{3RT\rho}{b} \left[a + \ln \eta^* + 2 \ln M_f^* + \ln \frac{\pi A_m^3}{24kTM_g^2 s_m^2} \right] \tag{88}$$

This equation can then be solved for η^*:

$$\eta^* = \frac{24kTM_g^2 \cdot s_m^2}{\pi A_m^3 M_f^{*2} e^a} \cdot e^{bM_f^*/3RT\rho} \tag{89}$$

Here η^* must increase exponentially with M_f^*. Such a relationship is plausible on the basis of the results already obtained[33].

Just as important as Equation (89) are the limitations of its validity range The derivation just given for (89) is only valid when: (1) the empirical relationship (33) is fulfilled and (2) when M_f^* is at least 3 times smaller than M_f, *i.e.*, when the modulus $E^*(t)$, measured at time t, is at least 3 times larger than the static elastic modulus (74) (measured for very large values of t). If M_f^* is

not essentially smaller than M_f it is inadmissible to calculate the time required for M_f^* to change its configuration appreciably with the assumption of a free diffusion of the end points of M_f^*.

It must also be mentioned that the relaxation time spectrum is known to extend in the region of very short relaxation times beyond the limits of (33a), that it can be measured there experimentally, but that it is no longer admissible to consider those restoring force mechanisms provided with very short relaxation times all as due to an elastic probability mechanism symbolized by (76). In the region of very short relaxation times, presumably for $\tau < 10^{-3}$ second, less significance should be attached to computing E^* in Equation (75) or even the calculation of η^*.

In connection with (76), we find, in the validity range of this equation, the same chains which afford for short times t a small M_f^* and, therefore, a large $E^*(t)$, and for large times t, a large M_f^* and, therefore, small $E^*(t)$. [After a rapid deformation of the total linear chain, the improbable configurations imposed upon short linear sections (small molecular weights $M^*(t)$) disappear quickly, whereas the analogous improbabilities in large sections of the same molecule are retained longer, so that the latter improbabilities remain when the former have already disappeared.]

These happenings in one molecule qualitatively cause a time decrease of the elastic modulus $E^*(t)$. On the other hand, this empirical decrease (according to Equation (58)) has been described by a relaxation time spectrum (50) and (2a) and occasionally restoring force mechanisms working parallel to one another have been considered. Actually the course of (2a) and (50) can be obtained with corresponding restoring force mechanisms working both parallel and independent of one another. As has already been emphasized, restoring force mechanisms working in parallel are not the only possibility for obtaining the course (2a); there are a great many other, complex combinations which can also explain the phenomena. The derivation just given of (76) actually gives the course of (58), but does not proceed from mechanisms working parallel to, or independent of, one another, but from a complex total mechanism in which the rapidly relaxing elements are used in an interesting manner as subunits from which the slowly relaxing elements are built up. In any case, the mechanism explained with (76) can only in the highest symbolic way be said to be a set of parallel working independent mechanisms.

For this reason, it is very important that the derivation of the relationship between the elastic and viscous behavior carried out in the foregoing sections was based exclusively on the experimental fact of the time dependence of the elastic modulus according to (2a) and (3), and by no means on assumptions concerning the ways and means of how this time dependence is created. Since the derivation of the relationships has been kept independent of any model, all results, such, for example, as the calculation of the viscosity from the course of the elastic modulus, are independent of the particular considerations of the present section, in which the elastic modulus is based on a scale model.

The relaxation time of an individual restoring-force mechanism being determined by, and itself determining in part, the relaxation times of all the remaining restoring force mechanisms present in a material

An additional problem which arises from, and whose treatment is to some extent made possible by, the foregoing considerations may be stated briefly in the following. Assume that the relaxation time spectrum, *i.e.*, $dE_0/d\tau$, in

Equation (3) is given. The total elastic and viscous behavior of the material, as established above, is then completely determined. The mechanisms whose relaxation times lie between τ and $\tau + d\tau$, contributing the quantity $d\tau . dE_0/d\tau$ to the elastic modulus, can be correlated to a definite process occurring in the medium, *e.g.*, the change of the configuration of a specific part of a lattice link. This movement of the lattice link portion relative to its surroundings is a diffusion process, as described in Equation (77 ff); it depends, therefore, on the viscosity by which the embedding medium opposes this special process, and thus is determined itself by the relaxation time spectrum. In other words, each portion of the relaxation time spectrum is determined by the remaining portion of the relaxation time spectrum. The relaxation time for a particular force mechanism, on the one hand, through the viscosity determines the relaxation times of all the other force mechanisms and simultaneously, on the other hand, also through the viscosity itself, is determined by all the other relaxation times.

Haegel[34] had first noticed the characteristic that a given linear segment whose relaxation time is τ must, in order to accomplish relaxation, travel a path of length, h^*, that it is hindered thereby by other restoring force mechanisms, and that this hindering is due exclusively to those foreign mechanisms, whose interstitial distance is smaller or approximately equal to h^*.

For example, if the relaxation time τ of a mechanism, whose relaxation requires linear molecular sections to travel through a distance h^*, is given by (86) then η^*, *i.e.*, viscosity, by which the medium retards those particular mechanisms, would be given on the basis of (13) by:

$$\eta^* = \frac{1}{2(1+\mu)} \int_0^{\tau_{max}} \frac{dE_0}{d\tau} \tau d\tau \tag{90}$$

wherein τ_{max} equals the value of t calculated from (86) thus:

$$\eta^* = \frac{1}{2(1+\mu)} \int_0^{(\pi/24kT)\eta^*(h^{*4}/A_m)} \frac{dE_0}{d\tau} \tau d\tau \tag{91}$$

The evaluation of this equation, for example, by using Equation (50) for $dE_0/d\tau$, which at least approaches correctness, is impeded in that the value of the integral (91) is very sensitive to the change of the value substituted for τ_{max}, whereas, at the same time, it appears to be difficult to find a fundamentally accurate expression for this. But it is clear that relationships of the type (90) must exist and that their study and evaluation will give further insight into the details of the origin of elastic-mechanical behavior in high and low polymer materials.

SUMMARY

In Part I of this work, the occurrence of a relaxation time spectrum in high-polymer materials was described, and a quantitative expression for the relaxation time spectrum for rubber and rubberlike materials was found, based on the creep curve observed for these materials, *i.e.*, the distribution density was given with which the partial elastic moduli are distributed among the relaxation times.

In the present paper, conclusions have been derived regarding the elastic and viscous behavior of the materials on the basis of the relaxation time spectrum reported.

It has been found that the expected creep curve in such a material, *i.e.*, the curve of the change of length after a definite time at a constantly held stress,

must be practically identical with the reciprocal value of the elastic modulus E, which can be determined as a time function from the decrease of stress after rapid deformation.

The E modulus observed at time t after rapid deformation is a function of all portions of the relaxation time spectrum in such a way, however, that $E(t)$ is mainly determined by those portions of the spectrum, for which the relaxation time τ is greater than t.

The accuracy with which the distribution of the partial elastic moduli can be computed from the available experimental data is not equally large for all regions of the relaxation time spectrum. The possible errors lie both in the region of very large relaxation times τ and very small times. But it appears that the error in the E modulus and in the viscosity, due to the contributions of the inaccurately known portions of the spectrum, is small in all cases and that these inaccuracies represent only a small constant added to the E modulus and the viscosity in the field of practical interest.

The dynamic elastic modulus, in the frequency range 10^{-2} to 10^{4} per second, on the basis of the relaxation time spectrum, is found experimentally to be almost independent of the period.

On the other hand, the dynamic viscosity increases proportionally to the period.

For a period T_s, those restoring force mechanisms whose relaxation time is somewhat but not much smaller than T_s contribute almost entirely to the magnitude of the dynamic viscosity.

The amount of heat developed in a test-sample per cc. and per second by periodic displacement increases proportional to the frequency of the applied deformation. The proportionality factor can be calculated from the deformation-time curve observed at constant load, *i.e.*, from the creep curve.

It is evident that the distribution density in the relaxation time spectrum in the region $\tau < 10^{-4}$ second increases somewhat more rapidly than the extrapolation of the formula valid for the region 10^{-2} to 10^{4} second would indicate.

It was shown that those restoring force mechanisms for which the relaxation time is greater than 10^{-2} second are probability mechanisms, whereas in the case of shorter relaxation times, energy mechanisms occur in increasing proportions in addition to, or in place of, the probability mechanisms.

The occurrence of probability mechanisms having the relaxation time t^* is to be interpreted in such a way that linear sections of molecular weight M^*, which must be smaller than the molecular weight M_f of the lattice link or of the total molecule, need a time t^* to change their configuration or orientation noticeably in the interior of the mass in which they are embedded. Accordingly, a relationship between t^* and M^* can be given. t^* depends on the viscosity η^* by which the embedding medium opposes a Brownian movement by the linear section of molecular weight M^*.

Conclusions can be drawn that η^* increases rapidly with M^*, *e.g.*, exponentially.

Furthermore, as is shown, the relaxation time of a restoring force mechanism considered not only through its contribution to the viscosity determines the relaxation times of all the other restoring force mechanisms, but also by their contributions to the viscosity is itself determined by the total of all the other relaxation times.

NOTE ADDED TO THE TRANSLATION

By Werner Kuhn

In the preceding paper, the existence of a relaxation time spectrum in soft vulcanized rubber, in particular in the region between 10^{-3} to 10^{4} seconds, was explained in the following way:

1. Linear chain segments of molecular weight M_f^* smaller than M_f (the molecular weight of the lattice link, terminated by vulcanization points) need a time t^* to change their configuration or orientation noticeably in the interior of the mass in which they are embedded.

2. The time t^* is equal to the time a filament of molecular weight $M_f^*/2$ would require to travel by Brownian movement, *i.e.*, by diffusion in the embedding medium, through a distance $h^*/3$ where h^* is the normal mean end-to-end distance of a statistically coiled chain or chain sequent of molecular weight M_f^*.

3. The viscosity (η^*) which the embedding medium (softly vulcanized bulk rubber) opposes to the diffusion of a linear chain of molecular weight M_f^*, depends on M_f^*. The force K, necessary to move a linear chain of molecular weight M_f^*, *viz.*, of length $N_m^* A_m = (M_f^*/M_g \cdot s_m)A_m$ through the medium with a velocity u is:

$$K = N_m^* A_m \cdot \frac{3\pi}{2} \mu \eta^* \tag{92}$$

Equation (80) gave this force for a linear chain of molecular weight $M_f^*/2$. Therefore, the diffusion constant D^* of a filament of molecular weight M_f^* will in analogy to (82) be equal to:

$$(D^*)_{M_f^*} = \frac{2kTM_g s_m}{3\pi M_f^* \cdot A_m (\eta^*)_{M_f^*}} \tag{93}$$

4. If the time dependence of the restoring force after sudden deformation of a test-sample of weakly vulcanized rubber is to be explained in the way just presented (Equation (89)), the viscosity which soft bulk rubber opposes to diffusion of a linear filament of molecular weight $M_f^*/2$ should be given by Equation (89), and the viscosity opposed to the translation of a filament of molecular weight M_f^* correspondingly by:

$$(\eta)_{M_f^*} = \frac{6kT}{\pi} \frac{M_g^2 s_m^2}{M_f^{*2} A_m^3} \cdot e^{-a} \cdot e^{2bM_f^*/3RT\rho} \tag{94}$$

where a and b are the constants characterizing the creep curve (Equation (58)).

It has lately been possible to verify the assertion made by Equation (94) or (93) by comparison with experiments on diffusion of substances of various molecular weights in soft vulcanized rubber[35].

Dependence of η on M_f^* according to Equation (94), i.e., according to the model interpretation of the relaxation time spectrum

On the one hand, the actual value of the constants a and b in Equation (94) are, in the case of a soft vulcanized rubber, according to Table I, *e.g.*, $a = 15$, $b = 10^8$ dynes per sq. cm., while the other constants are, in the case of rubber: $A_m = 13.10^{-8}$ cm., $s_m = 3$, $Mg = 68$, $\rho = 1$. Thus, putting $M_f^* = 500$, if (94), *i.e.*, the model interpretation of the relaxation time spectrum of rubber,

holds true, there would be expected by introducing the numerical values into (94):

$$(\eta)_{500} = 7.2 \text{ poises} \tag{95a}$$

and similarly, putting $M_f^* = 5000$:

$$(\eta)_{5000} = 1.5 \times 10^4 \text{ poises} \tag{95b}$$

The viscosity which soft vulcanized rubber opposes to the diffusion of a linear molecule of molecular weight $M = 500$ should thus, at room temperature, equal 7.2 poises, while the viscosity of the same rubber, for a filament of molecular weight $M = 5000$, should be 1.5×10^4 poises (2000 times as high as for $M = 500$). These viscosity values according to (95a) and (95b) are shown as encircled points, marked A and B, in Figure 4.

Dependence of η on M according to actual diffusion of molecules of various molecular weight, dissolved in rubber

The diffusion of substances of various molecular weights, *e.g.*, of colored substances, dissolved in pure soft vulcanized rubber, has been determined experimentally[36], with special care by Grün[37]. In these experiments, a strong decrease of the diffusion constant with increasing molecular weight M was observed. By a relation equivalent to (93) namely, by the relation:

$$D = \frac{kT}{6\pi\eta\tau} \tag{96}$$

where τ is the approximate radius of the diffusing molecule, the viscosity η which pure rubber opposes to the diffusion of the various dissolved substances can be computed. These values are plotted as simple dots in Figure 4.

It is seen from this figure that the dependence of η on M, determined from the diffusion of colored solutes in rubber (simple dots) coincides well with points A and B (encircled points of Figure 4), *i.e.*, with the dependence according to Equation (94) following from the model interpretation of the creep curve (Equation (58)). The coincidence in the last analysis represents a quantitative correlation between the creep curve of rubber and the diffusion constants of foreign substances dissolved in rubber. *The concordance can be considered as a*

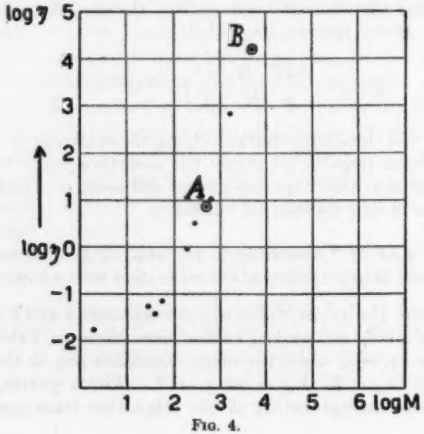


FIG. 4.

strong argument in favor of the model interpretation given in the section on the significance of the relaxation time spectrum of the present paper for the relaxation time spectrum of rubber in the region $10^{-3} < t < 10^{4}$ second.

Simple dots (·) show the viscosity η which pure rubber opposes to the diffusion of dissolved colored substances as function of the molecular weight M of the diffusing substances, calculated from diffusion measurements by F. Grün, using Equation (96).

Encircled dots (⊙) show the viscosity η which pure rubber opposes to the change of the shape of a linear segment of the rubber molecule itself as a function of the molecular weight M^* of the linear segment which is moving, calculated from Equation (94), using the values $a = 15$, $b = 10^8$ dynes per sq. cm. of the creep curve, characteristic of weakly vulcanized rubber according to Table I. Point A corresponds to Equation (95a), point B to Equation (95b).

REFERENCES

[1] The use by Kuhn of the term *Relaxationszeitspektrum* has been translated literally as *relaxation time spectrum*, and is identical in meaning with the expression *distribution of relaxation times* as used by Tobolsky and coworkers [Translators].
[2] Kuhn, *Z. physik. Chem.* **42B**, 1 (1939); *Z. angew. Chem.* **52**, 289 (1939); Bennewitz and Rötger, *Physik.-Z.* **40**, 416 (1939).
[3] Kuhn, *Z. physik. Chem.* **42B**, 1 (1939); *Z. angew. Chem.* **52**, 289 (1939).
[4] Kuhn uses the term *Zusammenhaltmechanism*, which has been translated as *restoring force mechanisms*, *i.e.*, of the Maxwell or Kelvin kind.
[5] Kuhn, *Z. physik. Chem.* **42B**, 1 (1939).
[6] Kuhn, *Z. angew. Chem.* **52**, 289 (1939).
[7] Kuhn, *Z. angew. Chem.* **52**, 291 (Fig. 1) and 292 (Fig. 4) (1939).
[8] Smekal, *Z. physik. Chem.* **44B**, 286 (1939); Jenckel, *Z. physik. Chem.* **184A**, 309 (1939); Frenkel and Obrastzov, *J. Phys. Acad. Sci. USSR* **2**, 1931 (1940); Holsmüller, and Jenckel, *Z. physik. Chem.* **186A**, 359 (1940); Taylor and Doran, *J. Am. Ceramic Soc.* **24**, 103 (1941); Ferry, *J. Am. Chem. Soc.* **64**, 1323 (1942); *Ann. N. Y. Acad. Sci.* **44**, 313 (1943); Taylor, *J. Applied Physics* **12**, 753 (1944); Tobolsky and Andrews, *J. Chem. Physics* **13**, 3 (1945).
[9] The following recently published references are suggested to bring the reader up to date: Gross, *J. Applied Physics* **18**, 212 (1947), **19**, 257 (1948); Gross and Pelzer, *J. Applied Physics* **22**, 1035 (1951); Ferry and Williams, *J. Colloid Sci.* **7**, 347 (1952); Ferry, and others, *J. Applied Physics* **22**, 717 (1951); Tobolsky, *J. Am. Chem. Soc.* **74**, 3786 (1952).
[10] Kuhn, *Helv. Chim. Acta* **30**, 487 (1947).
[11] Van der Wijk, *Proc. Rubber Tech. Conf. London* **1938**, p. 985.
[12] Hauk and Neumann, *Naturwissenschaften* **26**, 365 (1938).
[13] Haegel, *Helv. Chim. Acta* **27**, 1669 (1944).
[14] Grün and Haegel, unpublished experiments.
[15] Simha, *J. Applied Physics* **13**, 201 (1942).
[16] Alfrey and Doty, *J. Applied Physics* **16**, 700 (1945).
[17] Brenschede, *Kolloid-Z.* **104**, 1 (1943).
[18] The same behavior is described in connection with other authors' observations; for example, measurements of natural and synthetic rubbers by Tobolsky and Andrews (*J. Chem. Physics* **13**, 3 (1945)) and measurements by Kobeko, Kuvshinskii, and Gurevitch (*Techn. Physics USSR* **4**, 622 (1937)) described by Tobolsky and Eyring (*J. Chem. Physics* **11**, 125 (1943)).
[19] To describe the dependence of distribution density more exactly than in the approximation (55), the value (51) has to be used instead of (54*c*).
[20] See preceding paper in this issue.
[21] Equation 50 and Figure 1 of Part I.
[22] Van der Wijk, *Proc. Rubber Technol. Conf. London* **1938**, p. 985. From the dimensions of the apparatus of van der Wijk, a period of about 100–200 seconds can be estimated. If this value is substituted in (63), a viscosity of about (4–10) $\times 10^8$ poises is obtained for rubber instead of (63a) and (63b).
[23] *Helv. Chim. Acta* **30**, 839 (1947).
[24] Kuhn, *Kolloid-Z.* **78**, 258 (1936); *Z. angew. Chem.* **49**, 858 (1936); **51**, 640 (1938); *Kautschuk* **14**, 182 (1938), and later publications. See also the earlier qualitative contributions of E. Wöhlisch, K. H. Meyer, E. Guth, and H. Mark.
[25] Kuhn, *J. Polymer Sci.* **1**, 380 (1946).
[26] Kuhn uses the term *Fadenknäuel*, which has been translated literally as *linear coil*, and which is believed to be equivalent to random molecular configuration of a lattice link.
[27] Kuhn, *Z. angew. Chem.* **51**, 640, 647 (1938).
[28] Rossi, *Rend. accad. Napoli* **16**, 125, 142, 207 (1910); *Nuovo cimento* **20**, 226 (1910). For theoretical foundations, see Kuhn and Grün, *Kolloid-Z.* **101**, 248 (1942); Thibodeau and McPherson, *J. Research Natl. Bur. Standards* **13**, 887 (1934).
[29] Grün, F., and Haegel, J., unpublished experiments.
[30] Kuhn, Suhr, and Ryffel, *Helv. Chim. Acta* **14**, 497 (1941).
[31] Kuhn uses the term *Grundmolekül*, which seems to correspond to the recently adopted American term *mer*, the simplest repeating unit in a polymer.
[32] Kuhn and Kuhn, *Helv. Chim. Acta* **26**, 1394 (1943).
[33] *Z. physik. Chem.* **42B**, 1 (1930); *Z. angew. Chem.* **52**, 289 (1939). To describe the dependence of distribution density more exactly than in the approximation (55), the value (51) has to be used instead of (54*c*).
[34] Haegel, *Helv. Chim. Acta* **27**, 1669 (1944).
[35] Kuhn, *Makromol. Chem.* **6**, 224 (1951).
[36] See Part I of this series. Haegel, *Helv. Chim. Acta* **27**, 1669 (1944).
[37] Grün, *Exper.* **3**, 490 (1947).

HYDROGENATED SYNTHETIC ELASTOMERS *

R. Vernon Jones, C. Wayne Moberly, and W. B. Reynolds

Research Division, Phillips Petroleum Co., Bartlesville, Oklahoma

Several years ago the Phillips Petroleum Company initiated a study of the properties of hydrogenated synthetic elastomers. The result of this investigation has been the development of a series of thermoplastic hydrogenated polymers, Hydropols, which have certain unusual properties not found in other available plastics.

Prior to this investigation, little was known about hydrogenated synthetic elastomers. The hydrogenation of natural rubber had been fairly well investigated since Berthelot[1] heated rubber with concentrated hydriodic acid in a bomb tube and obtained a mixture of high boiling paraffins. Harries[2] stimulated the work of Staudinger and Fritschi[3] and Pummerer and Burkard[4] by his statement, "It would be of great importance to be able to carry out the reduction of rubber, because hydrorubber probably distills unchanged in a high vacuum, and therefore its constitution could be determined for certain." This hydrogenation of rubber was simultaneously accomplished in 1922 by Staudinger and Fritschi[3] using a platinum catalyst dispersed in purified rubber at 270° C and 93 atmospheres of hydrogen pressure for 10 hours, and by Pummerer and Burkard[4] using dilute solutions of depolymerized rubber in methylcyclohexane with a platinum catalyst at ordinary temperatures and atmospheric pressures.

These and subsequent studies were made for the purpose of establishing the structure of rubber or for preparing a synthetic lubricant. Memmler[5] points out that "all of the methods for the hydrogenation of rubber, disregarding the method involving the severe reaction at 270° C, are unreliable and have much to be desired". The same may be said for the hydrogenation of synthetic elastomers. Staudinger[6] describes hydrobutadiene rubber as having the same properties as hydrorubber, *i.e.*, "an amorphous, easily soluble, sirupy mass". Several patents disclose the hydrogenation of synthetic elastomers, but only Morris and Van Winkle[7] describe actual examples, and their work relates to hydrogenated polymeric methylpentadienes. Gruntfest and Biggs[8] reported a study of the structure of butadiene polymers and copolymers as indicated by the properties of very small samples of the hydrogenated materials.

It is apparent that little information has been published concerning the physical properties of hydrogenated synthetic elastomers. Thomas and coworkers[9] concluded that the chemical unsaturation, which is so important from the standpoint of permitting vulcanization to take place, is also the greatest weakness of the natural rubber molecule. Furthermore, it was known that very little unsaturation (2 to 3 per cent) is necessary for vulcanization[10].

Early experiments of the present study were carried out using a butadiene-styrene (72/28) copolymer prepared at 41° F by emulsion polymerization. Care was taken to protect the latex from air by blanketing it with nitrogen,

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 5, pages 1117–1122, May 1953.

since no antioxidant was used. The latex was coagulated with methanol and salt, and the rubber was dried and purified by dissolving and reprecipitating from benzene solution. A methylcyclohexane solution of this rubber was hydrogenated in the presence of a reduced nickel-on-kieselguhr catalyst at 300° F for 8 hours. The inherent viscosities of the polymers before and after hydrogenation were 1.85 and 1.80, respectively, indicating that possibly little or no degradation was caused by this treatment. The residual unsaturation, determined by iodine monochloride titration[11], was 73.8 per cent for the polymer before hydrogenation and 60.8 per cent after hydrogenation. Evaluation of

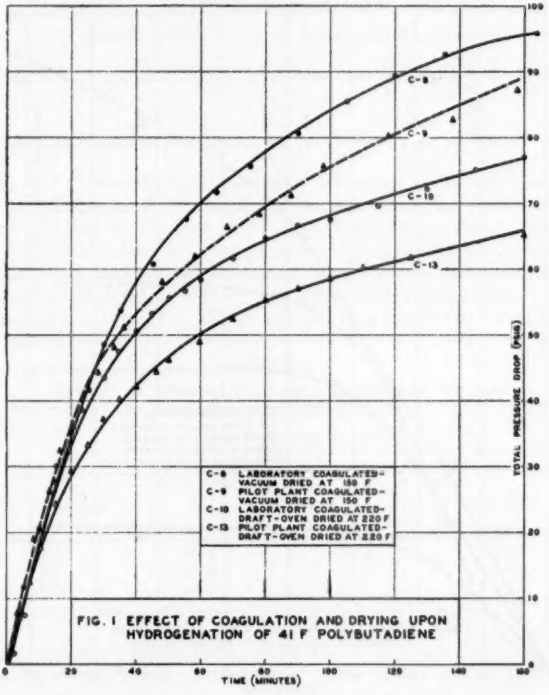


FIG. 1 EFFECT OF COAGULATION AND DRYING UPON HYDROGENATION OF 41 F POLYBUTADIENE

the physical properties of this product in tread and carcass recipes indicated that the hydrogenated polymer was somewhat improved in low temperature properties, but was otherwise not outstanding. However, it was soon demonstrated that polymers and copolymers of butadiene when hydrogenated to residual unsaturations of less than 50 per cent, produce a class of thermoplastics of outstanding freeze point, oil resistance, and tensile strength. These properties suggested their application as arctic plastics for use in rain wear, protective covering, fuel storage cells, wire coating, etc. Subsequent work involving detailed study of the preparation and evaluation of these and other hydrogenated polymers as arctic plastics was carried out.

PROCESS

Early in the investigation it was found that the treatment of the polymer prior to hydrogenation had considerable effect on the ease and extent of hydrogenation. The special precaution of omitting antioxidants and protecting the rubber with a blanket of nitrogen was found to be less desirable than the use of antioxidants. Special reprecipitation of the rubber from benzene was not necessary. Satisfactory synthetic elastomers for hydrogenation could be prepared in the usual manner or by alcohol precipitation. The effect of various treatments of the polymer prior to hydrogenation is shown in Figure 1. Hydro-

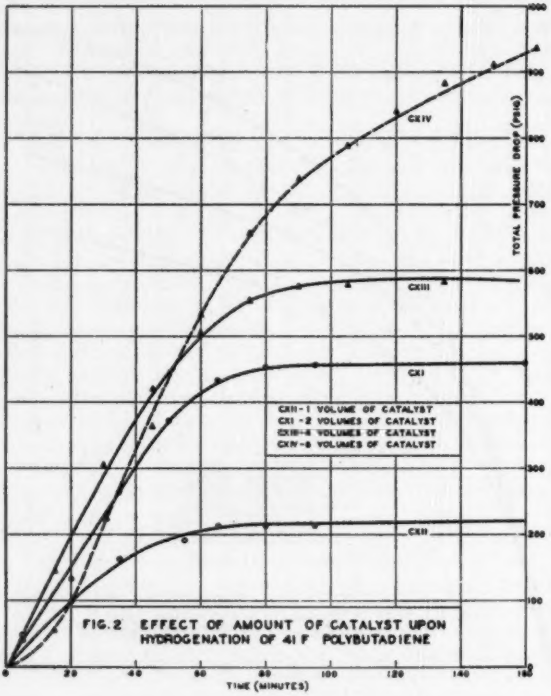


FIG. 2 EFFECT OF AMOUNT OF CATALYST UPON HYDROGENATION OF 41 F POLYBUTADIENE

genation of samples of 41° F emulsion polybutadiene differing only in the method of drying indicated that samples dried in a vacuum oven at 150° F hydrogenated to an appreciably greater extent than those dried in a forced draft oven at 220° F. A sample coagulated in the laboratory (alcohol-precipitated) and dried in the vacuum oven at 150° F was hydrogenated to give a product with an unsaturation of 29.1 per cent, whereas an identical sample coagulated (conventionally with salt-acid) in the pilot plant and dried in a forced draft oven at 220° F hydrogenated under similar conditions gave a product with an unsaturation of 43.4 per cent. Similar results were obtained with samples of other polymers.

The effect of the amount of catalyst on the extent of hydrogenation is shown in Figure 2. Samples of the same 25-Mooney, 41° F emulsion-polymerized polybutadiene were hydrogenated under similar conditions using increasing amounts of catalyst. Unsaturations of products obtained with varying amounts of catalyst are given in Table I.

Adding all of the catalyst initially in a batchwise hydrogenation was found to be superior to incremental addition of catalyst. These experiments were

TABLE I

EFFECT OF AMOUNT OF CATALYST ON HYDROGENATION OF 41° F POLYBUTADIENE

Units of catalyst[a]	Unsaturation of products (%)
1	61.9
2	36.2
4	17.0
8	0.7

[a] One unit of catalyst gives ratio by weight of 1 part of nickel to 4 parts of polymer.

made using 41° F emulsion-polymerized 30-Mooney polybutadiene. Hydrogenation was effected at 300° F and 500 pounds per square inch gauge, using one unit of catalyst in the first step. When hydrogen absorption ceased, a sample of the mixture was withdrawn and additional catalyst added to give a total of 2.7 units of catalyst for the second step. In the third and fourth steps, the total amount of catalyst was 8.7 and 12.5 units, respectively. The procedure was repeated at a hydrogenation temperature of 400° F. For comparison,

TABLE II

EFFECT OF TEMPERATURE AND METHOD OF ADDING CATALYST ON HYDROGENATION

	Percentage unsaturation		
	Batch addition of catalyst	Increment addition of catalyst	
	300° F		400° F
Units of catalyst[a]			
1	70.4	90.2	88.3
2.7	46.3	69.8	46.7
8.7	31.2	48.5	26.9
12.5	14.7	32.0	12.8

[a] One unit of catalyst gives ratio by weight of 1 part of nickel to 33 parts of polymer.

the same polymer was hydrogenated under the same conditions using 1, 2.7, 8.7, and 12.5 units of catalyst added initially. The results presented in Table II indicate that hydrogenation is much more effective when all of the catalyst is added initially.

Hydrogenation is most effective at very high temperatures. Three experiments carried out with 41° F emulsion polybutadiene under similar conditions except for temperature illustrate this effect (Table III).

TABLE III

EFFECT OF TEMPERATURE ON HYDROGENATION OF POLYBUTADIENE

Temp. of hydrogenation (°F)	Unsaturation of product (%)
300	34.6
350	25.6
450	9.5

Hydrogenation to a given unsaturation value can be accomplished with considerably less catalyst at higher temperatures. For example, hydrogenation of a 41° F emulsion polybutadiene at 500° F, using one unit of catalyst, gave a polymer of lower unsaturation than a comparable product obtained by hydrogenation at 350° F, with eight units of catalyst. The inherent viscosities of toluene solutions of products prepared at higher temperatures indicate that

TABLE IV

INHERENT VISCOSITIES OF HYDROGENATED POLYBUTADIENE SOLUTIONS IN TOLUENE AT 75° C.

Sample	Viscosity
Unhydrogenated control (41 ML-4)	1.78
Hydrogenated at 300° F (32.9% unsat.)	1.95
Hydrogenated at 400° F (16.5% unsat.)	1.93
Hydrogenated at 450° F (14.3% unsat.)	1.84
Unhydrogenated control (20 ML-4)	1.29
Hydrogenated at 500° F (9.8% unsat.)	1.24

there is little, if any, degradation of the polymer at hydrogenation temperatures up to 500° F (Table IV).

Both batchwise and continuous methods can be used for the hydrogenation of synthetic elastomers. Batchwise reactions can be carried out in conventional rocker-type or stirred autoclaves. A flow diagram of a continuous reactor is shown in Figure 3 and a photograph of a laboratory model in Figure 4.

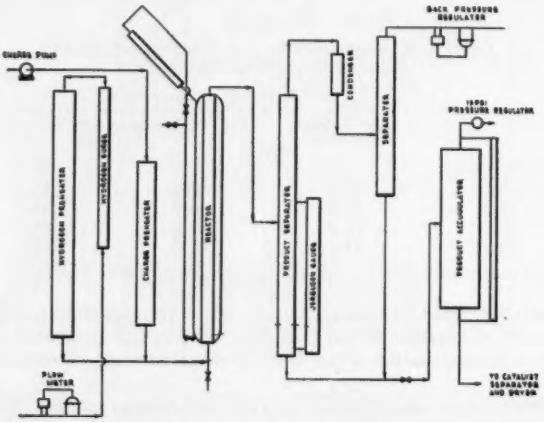


FIG. 3.—Continuous hydrogenation apparatus.

Most of the hydrogenations of the products reported in the present paper were carried out in a 5-gallon stirred autoclave. The polymer was dissolved in warm methyl cyclohexane or other suitable solvent to give a 5 to 6 per cent solution, which was charged to the autoclave along with the desired amount of reduced nickel-on-kieselguhr catalyst. After the system had been flushed with hydrogen, the reduction was carried out at the selected temperature and

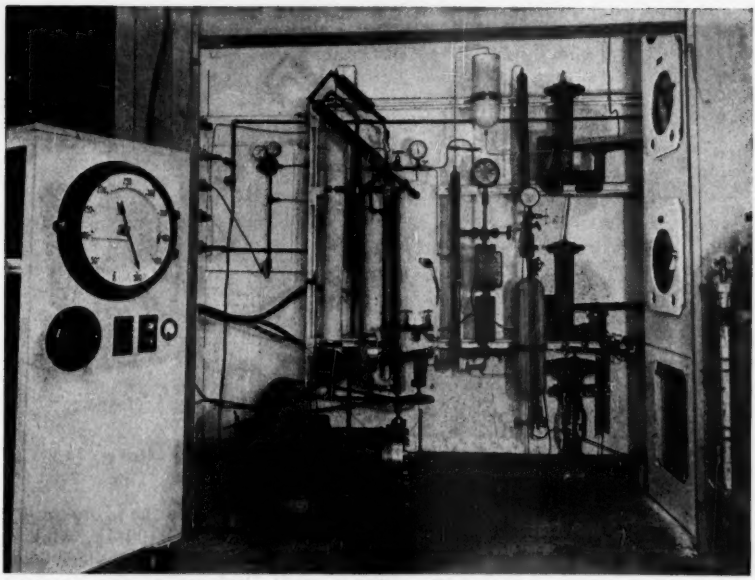


FIG. 4.—Continuous reactor for hydrogenation of synthetic elastomers.

pressure. Catalyst removal was by centrifugation or other means and the product was recovered by removing the solvent on a drum dryer.

PROPERTIES

The number of variables to be examined in studying hydrogenated polymers is large. Such factors as monomer types, polymerization process, and molecular weight influence the properties of the hydrogenated synthetic elastomers to a great extent. Furthermore, the degree of hydrogenation is of primary importance. After extensive exploratory work a 41° F polybutadiene rubber was selected for further study. Table V compares the properties of a typical hydrogenated polybutadiene plastic with polyethylene.

TABLE V

COMPARISON OF PROPERTIES OF A TYPICAL HYDROGENATED POLYBUTADIENE WITH MOLDING GRADE POLYETHYLENE

	Hydropol[13]	Polyethylene
Tensile strength (77–80° F, lb./sq. inch)	2,350	1,900
Elongation (77–80° F, %)	750	600
Stiffness modulus (77° F, lb./sq. inch)	15,000	20,000
Load deformation (%)	7.75 (77° F)	0.6 (122° F)
Hardness (Durometer)	78 A-2	98 A
Brittle point (° F)	<-100	>-100
Impact strength	Does not break	Does not break
Refractive index at 77° F	1.50	1.51
Molecular weight	Ca. 100,000	Ca. 18,000

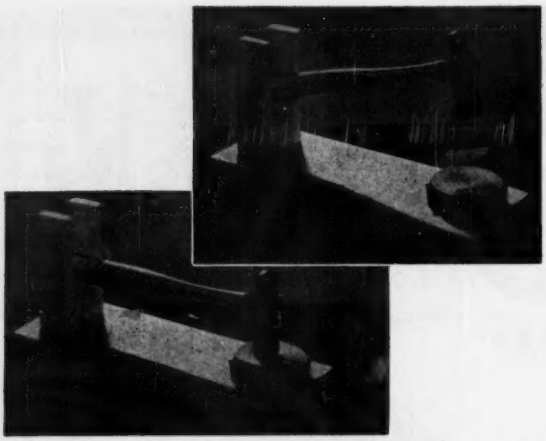


FIG. 5.—Hydropol (above) and polyethylene (left) disks cooled to −100° F and struck with hammer.

The excellent low-temperature properties are illustrated in the photographs. Figure 5 shows the shattering of a polyethylene disk at −100° F, while a similarly treated Hydropol disk remains intact. Likewise, polyethylene coating on wire cracks on flexing at −100° F, while Hydropol coating does not (Figure 6). No glassy-state transition was found for Hydropols of 7.2 and 21.3 per cent unsaturation at temperatures[17] down to −160° C.

Numerous evaluations of the physical properties of these plastics show that, in general, the stress-strain properties, swelling resistance, and ozone resistance

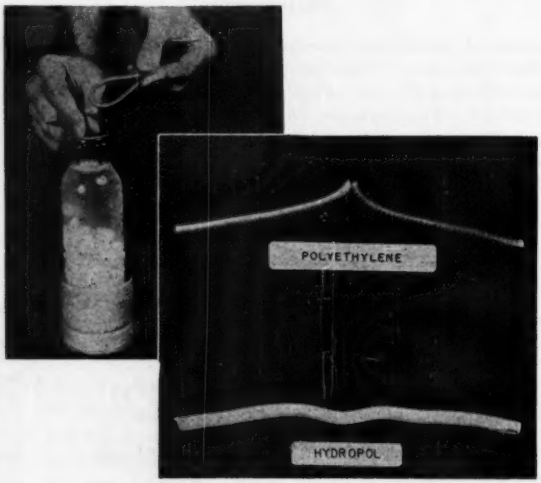


FIG. 6.—Effect of flexing wires coated with hydropol and polyethylene at −100° F.

are improved by increasing the degree of hydrogenation and (or) by using higher Mooney base stocks.

One of the salient features of the hydrogenated polymers is their susceptibility to vulcanization. The compounding recipe chiefly used in this work (Table VI) does not always give a tight cure, and the products are sometimes

TABLE VI

COMPOUNDING RECIPE FOR HYDROGENATED POLYBUTADIENE

	Parts
Hydropol plastic	100
Titanium dioxide	50
Zinc oxide	5
Age-Rite Alba	1
Stearite	2
Circo light oil	10
Sulfur	1
Santocure	1
A-32	0.32

Cured 45 minutes at 307° F

thermoplastic even after vulcanization. However, in spite of this, considerable cross-linking has occurred, as indicated by greater hardness and lower compression set. The properties of a typical compounded Hydropol plastic are shown in Table VII. The ability of Hydropol plastics to cold draw is illustrated in Table VIII. These data were obtained on an uncompounded stock where the material was stretched to varying lengths and allowed to relax.

TABLE VII

TYPICAL PHYSICAL PROPERTIES OF COMPOUNDED HYDROGENATED POLYBUTADIENE

Tensile strength (80° F, lb./sq. inch)	1580
Elongation (%)	380
Tear resistance (80° F, lb./inch)	220
Resilience (%)	81.2
Cold compression set (−35° F) (%)	87.6
Gehman freeze point (° F)	−72
Swelling in 70/30 isooctane/toluene (70° F, %)	98.6
Ozone resistance	Excellent

TABLE VIII

TENSILE STRENGTH OF ORIENTED HYDROGENATED POLYBUTADIENE

Stretched (%)	Elongation after relaxation (%)	Tensile strength[a] (lb./sq. inch)	Elongation (%)
0	0	3,930	700
100	20	3,320	490
200	70	4,360	270
300	140	5,450	220
400	200	7,770	100
500	250	10,730	85
550	300	10,820	85

[a] Obtained on dumbbell strips at 80° F

The excellent electrical properties of the Hydropol plastics, combined with their low temperature properties, indicate that they should be unexcelled for wire coating. These properties are shown in Table IX in comparison with polyethylene.

TABLE IX

COMPARISON OF ELECTRICAL PROPERTIES OF HYDROGENATED POLYBUTADIENE AND POLYETHYLENE
(Typical test values)

	Hydropol[13]	Polyethylene
Dielectric constant		
1 kc.	2.48	2.3
1 mc.	2.42	2.3
Power factor		
1 kc.	≈0	0.0005
1 mc.	<0.0016	0.0005
Water absorption (%)	0.0343	0.005
Flammability (in./min.)	1.53	1.1

The plasticity curves of several Hydropol plastics have been prepared according to the method of Willert[14]. These curves are shown in comparison with those of various thermoplastic resins in Figure 7. It will be noted that the plasticity of a Hydropol plastic prepared from a low Mooney polybutadiene is very high at relatively low temperatures. Although the products prepared

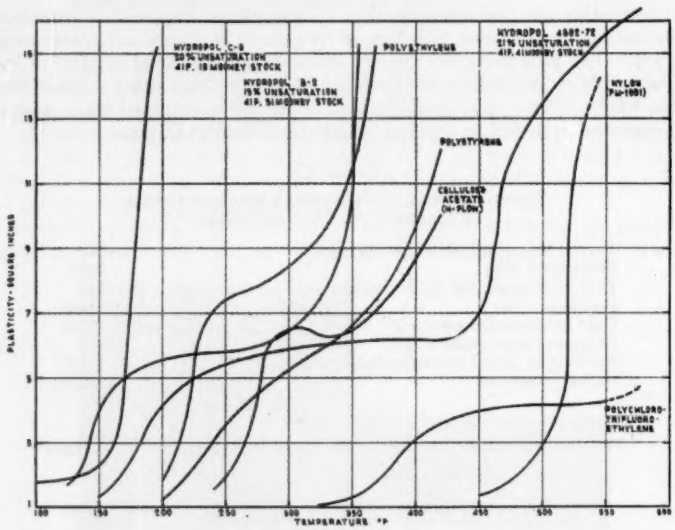


FIG. 7.—Plasticity curves for various thermosetting resins.

from higher Mooney polybutadiene initially soften at temperatures around 150° F, their plasticities remain fairly low until much higher temperatures are reached.

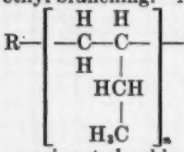
STRUCTURE

Hydrogenation of synthetic elastomers is a valuable tool for studying the structure of these polymers by infrared and x-ray techniques. Because the infrared spectrum of a product may be used as a means of identifying functional groups associated with its molecular structure, the spectra of unhydrogenated

FIG. 8.—Infrared spectra of emulsion-polymerised polybutadiene and various Hydropol plastics.

emulsion-polymerized polybutadiene and samples at various stages of hydrogenation have been obtained and studied. The spectrum of emulsion-polymerized polybutadiene is well known and is consistent with the structure expected from 1,2- and 1,4-additions to the butadiene unit.

The spectrogram of such a sample is shown in Figure 8, A. Many absorption bands of this spectrum have been correlated with structural groups[15] and are so indicated. Figure 8 (*B*, *C*, and *D*) shows the spectra of hydrogenated emulsion polybutadiene with unsaturation values[11] of 62, 25, and 7 per cent, respectively. It is evident that, as hydrogenation proceeds, the absorption bands at 6.1, 10.1, 10.3, and 11 microns, correlated with unsaturation, disappear. Although both the vinyl side groups and the internal bonds appear to hydrogenate simultaneously, there is some indication that the vinyl side groups hydrogenate more rapidly. However, even at only 20 per cent residual unsaturation, vinyl side groups remain. As unsaturation decreases a set of absorption bands characteristic of paraffin structures appears and increases in intensity with hydrogenation. These absorption bands appear at 7.25, 12.7, 13, and 13.7 to 13.9 microns. The 7.25-micron band is clearly characteristic of isolated $-CH_2$ groups and the 13.7- to 13.9-micron absorption is due to $-CH_2-$ sequences. Although the absorptions at 12.7 and 13 microns may be characteristic of ethyl branching, this correlation must be considered only tentative because of the lack of reference spectra of high molecular weight compounds with ethyl branching. A spectrum of poly-(1-butene) believed to have the structure



R gives a strong absorption band at 13.02 microns with a prominent shoulder at 12.7 microns.

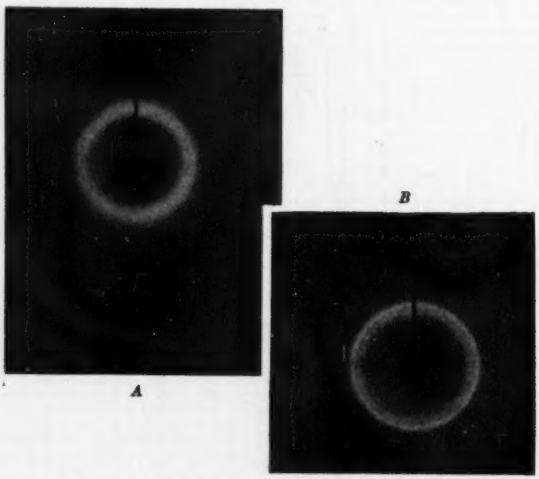


FIG. 9.—X-ray diffraction patterns of polybutadiene.
A. At room temperature
B. At dry ice temperature

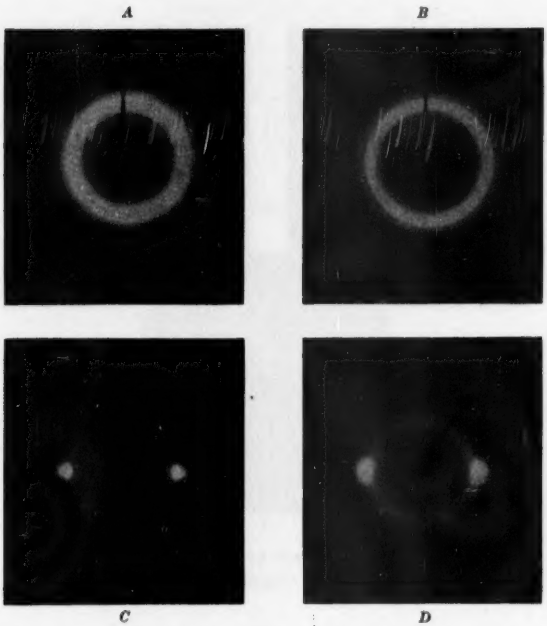


FIG. 10.—X-ray diffraction patterns of hydropol.

A. Room temperature
B. Dry-ice temperature
C. Stretched to 700%
D. Relaxed from 700% but retaining 300% permanent set

The very weak absorption band at 10.2 to 10.4 microns may not be due to remaining internal double bonds, as a weak absorption band might be expected in this region if isolated —CH_2— groups (R—C(R)—CH_2—C(R)—R) existed in the hydrogenated polymer.

X-ray diffraction patterns of polybutadiene and Hydropol are shown in Figures 9 and 10. The patterns for polybutadiene show that a considerable amount of ordering takes place when the sample is cooled to dry ice temperature. For the Hydropol about the same amount of ordering is present at room temperature as for the cooled polybutadiene, but cooling the Hydropol to dry ice temperature causes only a very slight increase in this ordering. Figure 10 *C*, shows the diffraction pattern of Hydropol obtained while the sample was held under tension at an elongation of about 700 per cent. This pattern shows marked preferred orientation and a repeat distance along the direction of stretch of about 2.4 A. When the tension was released, the sample was found to have acquired a permanent set of about 300 per cent. A diffraction pattern for the relaxed specimen is shown in Figure 10, *D*. This pattern indicates that a considerable amount of permanent preferred orientation resulted from the

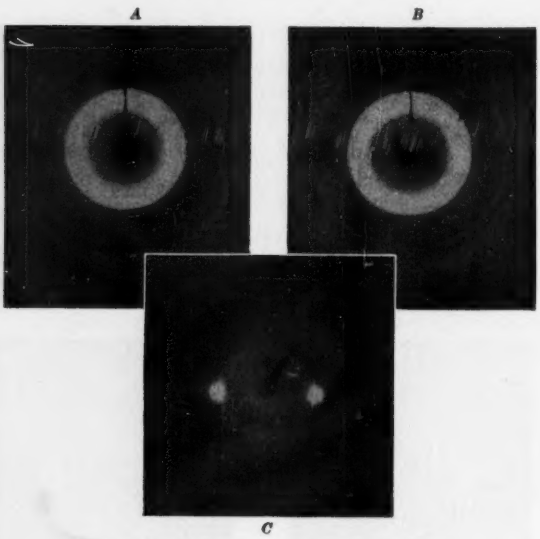


FIG. 11.—X-ray diffraction patterns of polyethylene.
A. Room temperature. *B*. Dry-ice temperature. *C*. Stretched

elongation, substantiating the observations on orientation presented in Table VIII.

Figure 11 shows x-ray diffraction patterns of polyethylene for comparison with those of Hydropol. These demonstrate the well-known crystallinity of this material and its marked orientation on stretching. The repeat distance along the direction of stretching is essentially the same as that for Hydropol.

Table X gives the crystal lattice spacings obtained from the x-ray diffraction patterns of Figures 9, 10, and 11.

TABLE X

CRYSTAL LATTICE SPACINGS

	Room temp. A.	Dry-ice temp. A.
Polybutadiene, 95.3% unsaturation		
Diffuse ring	4.48	4.33
Sharp ring	—	3.93
Hydrogenated polybutadiene, 3.3% unsaturation		
Strong sharp ring	4.10	4.08
Weak sharp ring	3.93	3.91
Very weak ring	2.47	2.46
Polyethylene		
Very strong	4.08	4.04
Strong	3.91	3.62
Weak	2.99	2.90
Medium	2.45	2.43
Weak	2.22	2.23
Weak	—	2.14

ACKNOWLEDGMENT

The authors are grateful to the late Walter A. Schulze for suggesting this problem and for his continued advice and encouragement relating to the work. They wish to thank J. F. Svetlik for compounding and evaluations, Vernon Thornton for spectrographic analyses, Robert Q. Gregg for the x-ray diffraction work, and the Plastics Laboratory of Princeton University for cooperation on certain evaluations.

REFERENCES

[1] Berthelot, *Bull. soc. chim.* [2], 11, 33 (1869).
[2] Harries, "Untersuchungen uber die natürlichen und künstlichen Kautschukarten", Julius Springer, Berlin, 1919, p. 48.
[3] Staudinger and Fritsche, *Helv. Chim. Acta* **5**, 785 (1922).
[4] Pummerer and Burkard, *Ber.* **55**, 3458 (1922).
[5] Memmler, "Science of Rubber", Reinhold Publishing Corp., New York, 1934, p. 229.
[6] Staudinger, *Helv. Chim. Acta* **13**, 1324 (1930).
[7] Morris and Van Winkle (to Shell Development Co.), U. S. patent 2,449,949 (Sept. 21, 1948).
[8] Gruntfest, I. J., and Biggs, B. S., Bell Telephone Laboratories, private communication, Dec. 1943.
[9] Thomas, Lightbown, Sparks, Frolich, and Murphree, *Ind. Eng. Chem.* **32**, 1283 (1940).
[10] Spence and Scott, *Z. Chem. u. Ind. Kolloide* **8**, 304 (1911); Boggs and Blake, *Ind. Eng. Chem.* **22**, 748 (1930); Brown and Hauser, *Ind. Eng. Chem.* **30**, 1291 (1938).
[11] Lee, Kolthoff, and Mairs, *J. Polymer Sci.* **3**, 66 (1948).
[12] Wood, L. A., National Bureau of Standards, private communications, May 28, 1952 and July 17, 1952.
[13] Maxwell, Brice, Princeton University, private communication, Jan. 14, 1952.
[14] Willert, *India Rubber World* **124**, 324 (1951).
[15] McMurry and Thornton, *Anal. Chem.* **24**, 318 (1952).

DIAZO-INITIATED POLYMERS

PREPARATION, PROPERTIES, AND EVALUATION *

J. M. Willis, Glen Alliger, B. L. Johnson, and W. M. Otto

Chemical and Physical Research Laboratory, The Firestone Tire and Rubber Co., Akron, Ohio

Throughout the great majority of the many investigations on rubberlike synthetic polymers, the initiators employed have been peroxides, either water-soluble (potassium persulfate being the chief example) or oil-soluble, such as benzoyl peroxide or diisopropylbenzene monohydroperoxide. The most notable departure from these initiators has been the use[1] of the diazothio ethers, 4-methoxybenzenediazomercapto-2-naphthalene (MDN) and 4-methylbenzenediazomercapto-2-naphthalene (TDN). These materials have proved to be suitable initiators and also to have some activity as modifiers. However, their possibilities have been explored principally at a polymerization temperature of 41° F. Thus, the field of initiators has been subject to less widespread investigation than most of the other variables in a typical synthetic rubber recipe.

The purpose of the present investigation was to develop different initiators, if possible, of a type which would lead to improvement of polymer structure at 122° F. It was felt from the outset that diazo-type compounds offered the best possibilities for development along these lines. During a preliminary survey of these materials, the object was to find examples which did not have the two disadvantages of the diazothio ethers—high cost and low stability.

The use of diazo-type compounds as polymerization initiators has been known for many years. The work of Buizov on the polymerization of butadiene with diazoaminobenzene is an example of this[2]. A number of patents have been issued relating to the use of diazo compounds in general as polymerization initiators or activators[3]. These patents, however, were directed toward improving the rate of polymerization, and did not indicate any outstanding improvement in polymer properties. After detailed study of the properties and reactions of diazo materials in general[4], stabilized salts of diazotized aromatic amines were selected as the specific type of compound with the greatest chance of success. The program was begun with the laboratory preparation and evaluation of diazo salts.

POLYMERIZATION WITH LABORATORY-PREPARED INITIATORS AT 122° F

Stable sodium diazotate salts were prepared from both aniline and *p*-nitroaniline by the method of Hickinbottom[5]. Polymerization studies were made at 122° F with these materials, using a 100-gram monomer charge of 70/30 butadiene-styrene in beverage bottles. Other ingredients were: 200 grams of water, 5 grams of soap flakes, and sodium hydroxide, the amount of which was

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 6, pages 1316–1322, June 1953. This paper was presented before the Division of Rubber Chemistry of the American Society at the meeting of the Division at Buffalo, N. Y., October 29–31, 1952. The work represents part of a research project sponsored by the Reconstruction Finance Corporation, Synthetic Rubber Division, in connection with the Government synthetic rubber program.

varied, as was the diazo initiator. Some of the later runs were modified with mixed tertiary thiols (MTM 4, Phillips Petroleum Co.). The results obtained in this series of runs are presented in Table I. There was a rate increase with increased initiator loading, and the *p*-nitroaniline derivative gave a faster reaction than the aniline derivative. It is of interest to note the ability of this system to initiate polymerization in the absence of thiol, which is not practical in the GR-S system using potassium persulfate. It is possible that the reaction proceeds by the hydrolysis of the diazo salt in aqueous solution to give the oil-soluble diazonium hydroxide, which then diffuses into the oil layer and decomposes to form free radicals. These aryl free radicals then initiate the polymerization.

TABLE I

POLYMERIZATION WITH LABORATORY DIAZO SALTS AT 122° F

Run no.	Diazo (part)	NaOH (part)	Time (hours)	Conversion (%)	%/hour	MTM 4, (part)	% gel[a]
			p-Nitroaniline derivative				
272	0.1	0.025	16.25	84	5.2	0	91.8
271	0.2	0.025	17	95	5.6	0	91.8
316	0.2	0.3	18.5	82	4.4	0.35	—
317	0.2	0.3	18.5	87	4.7	0	—
274	0.5	0.025	5.5	57	10.3	0	86.3
306	0.5	0.025	7	72.5	10.3	0	—
			Aniline derivative				
308	0.15	0.025	23	61	2.7	0.3	0.6
275	0.2	0.025	16	60	3.7	0	67.7
292	0.2	0.025	16	71	4.4	0	52.6
315	0.2	0.3	18.5	87	4.7	0	—
314	0.2	0.3	26	55	2.1	0.35	—

[a] Portion insoluble in toluene after 48 hours, unstirred.

The latex from a number of these runs was coagulated with salt-sulfuric acid solution and the polymer obtained was found to be of a characteristic deep red color, particularly in runs where dinitrochlorobenzene was used as the stopping agent. The product from later pilot plant batches in which sodium dimethyldithiocarbamate was used as the stopping agent was light brown when dry. The color is probably the result of unreacted diazonium intermediate coupling with other portions of the reaction system which may or may not be part of the polymer chain.

Polymer from run 308 (Table I) was compounded in a standard tread stock as follows:

Polymer	100
EPC black	45
Sulfur	1.7
Zinc oxide	2.4
Stearic acid	2.5
PBNA	0.6
Softener	6.6
Santocure	1.2

Physical tests on this stock compared to GR-S in the same recipe are presented in Table II. The results showed sufficient improvement over GR-S to warrant a much more detailed study of this type of initiation. Higher tensile strength and rebound and lower operating temperature were particularly noteworthy.

TABLE II

PHYSICAL PROPERTIES OF DIAZO-INITIATED POLYMERS

(70/30-BD/ST, standard tread stock)

Polymer	GR-S	X546[a]	37	35[b]	41[c]	308
Initiator	$K_2S_2O_8$	CHP[d]	Nitrazole-CF		AIBN[e]	Diaz. *p*-NA
Polymerization temp. (° F)	122	41	122	122	122	122
Williams plasticity (mm.)	3.41	—	3.55	4.06	4.10	3.50
Compd. Williams plasticity	3.21	—	3.57	3.78	4.25	—
Cure, min. at 280° F	400% Modulus (lb./sq. inch)					
40	900	300	950	1050	525	900
60	1475	950	1525	1650	1450	1575
80	1675	1300	1850	2025	1975	1725
120	1775	1675	2000	2200	2325	1950
	Tensile (lb./sq. inch)					
40	2750	1575	3450	3675	1950	3450
60	3450	3425	3900	3750	3650	3675
80	3225	3800	3725	3600	3800	3675
120	3300	3950	3475	3375	3750	3550
	Elongation (%)					
40	760	1100	760	750	840	760
60	660	810	640	620	660	570
80	600	730	580	550	600	570
120	580	670	540	500	530	530
	Rebound (%) (80-min. cure)					
72° F	47.5	49	46.5	48.5	45	49
212° F	56.5	58.5	61.5	63	63	62.5
	Flexometer tests					
Cold, 3-lb. penetration	52	50	47	48	49	—
Hot, 3-lb. penetration	78	74	70	67	62	—
Deflection (%)	21.3	21.3	19.3	20.0	—	18.7
Running temp. (° F)	266	270	245	240	232	260
Blowout time (min.)	15.5	17.5	30	31	32	—
	Forced vibrator at 100° C (80-min. cure)					
Dynamic modulus (lb./sq. inch)	177	182	175	180	170	—
Static modulus (lb./sq. inch)	115	122	150	140	140	—
Internal friction (lb./sq. inch)	5.0	5.1	4.5	4.2	4.8	—
	Cut growth (inches/hour) (80-min. cure)					
Normal	0.8	0.2	1.1	0.5	0.3	—
Aged 4 days at 212° F	4.6	4.3	10.5	4.3	3.0	12.0

[a] Cold rubber.
[b] O_2-free system.
[c] Dresinate-214 run.
[d] Cumene hydroperoxide.
[e] α,α-Azodiisobutyronitrile.

POLYMERIZATION WITH NITRAZOLE CF AT 122° F

In selecting a commercial diazo salt for use in runs on a larger scale, approximately twenty different examples were evaluated. They varied considerably in the number and type of substituents on their aromatic rings. Initiator

activity varied from zero up to a maximum reached by the following three samples:

Nitrazole-CF (General Dyestuff Corp.)
Fast Red GG salt (The Hilton-Davis Chemical Co.)
Fast Violet B salt (Otto B. May, Inc.)

The first two materials are stabilized salts of diazotized *p*-nitroaniline and the third of 6-benzoylamino-4-methoxy-*m*-toluidine. The material arbitrarily selected for the remainder of the study was Nitrazole-CF, because it was on hand in substantial quantity.

The laboratory evaluation of Nitrazole-CF proved that it was suitable in the polymerization recipe given above with only small changes. It proved desirable to use 0.3 part of sodium hydroxide in the recipe and, at this level, either 0.05 or 0.1 part of the Nitrazole was effective. The emulsifier level (soap flakes) was successfully reduced to 4 parts when the sodium hydroxide and

TABLE III

LABORATORY EVALUATION OF NITRAZOLE-CF CATALYST AT 122° F

Run no.	Nitrazole-CF (part)	Caustic NaOH (part)	Emulsifier soap flakes (parts)	Time (hours)	Conversion (%)
197–1	0.01	0.3	4	16	7
197–2	0.02	0.3	4	16	33
197–3	0.05	0.3	4	16	69
197–4	0.10	0.3	4	16	79
197–5	0.20	0.3	4	16	75
323–2	0.10	0.3	4	12.25	62.5
323–1	0.05	0.3	5	15.75	63.5
321–6	0.10	0.3	5	10.75	67.5
318	0.20	0.3	5	16	76
319	0.20	0.2	5	16	65
312	0.50	0.1	5	7	22
311	0.50	0.025	5	7	12
321–5	0.20	0.3	3	10.75	34
			Dresinate-731		
673	0.1	0.3	4	19.67	77.5
674	0.1	0.5	4	19.67	77.0
			KOH Dresinate-214		
671	0.1	0.3	4	19.67	46.5
672	0.1	0.5	4	19.67	60.0

Nitrazole were held at the 0.3 and 0.1 level, respectively. A more detailed study of polymerization rate as a function of Nitrazole-CF loading, using 0.3 part of sodium hydroxide and 4 parts of soap flakes, indicated an increase in rate up to 0.1 part, above which the rate remained constant. When Dresinate-731 or 214 (Hercules Powder Co.) was substituted for soap flakes, a somewhat reduced polymerization rate was obtained, particularly with the latter. A higher caustic loading was somewhat more effective. Details of these runs are recorded in Table III.

Stopping agent studies indicated that 0.2 part of di-*tert*-butylhydroquinone (Santovar-O, Monsanto Chemical Co.), 0.3 part of dinitrochlorobenzene (DNCB), or 0.1 part of sodium dimethyldithiocarbamate (ADAM) and 0.05 part of sulfur were effective in preventing increase in gel content or Mooney plasticity after their addition to the latex.

A study was made of the effect on the rate of polymerization of essentially complete removal of oxygen from the system. The technique used for loading an oxygen-free charge included boiling the distilled water used while saturating

it with lamp grade nitrogen, blowing all solutions with this nitrogen, and finally purging the bottle with nitrogen before adding the butadiene. Results of polymerizations in which oxygen-free and standard loadings are compared show a noticeable increase in reaction time for the former. This indicates that the oxygen does play a part in the Nitrazole recipe.

In an interesting comparison with the above data, a number of runs were made using α,α'-azodiisobutyronitrile (AIBN, Rohm & Haas Co.) as the initiator. This material is oil-soluble, compared to the water solubility of Nitrazole CF. In this case, the exclusion of oxygen from the system gave a small activating effect.

Physical tests of several of these polymers compounded in the standard tread stock (EPC black) are shown in Table II. In tensile strength, the diazo polymers are similar to X546 (cold rubber) which gives values 400 to 500 pounds per square inch higher than GR-S. The rebound, running temperature, blowout time, and internal friction are all excellent for the diazo polymers, and are superior to both X546 (LTP) and GR-S. In aged cut-growth resistance, the diazo polymer 37 is inferior, but this appears to be brought to the level of the controls by either an oxygen-free system or the use of Dresinate emulsifier. No difference is noted between the use of Nitrazole-CF and AIBN as far as physical properties are concerned.

Several other variables which may affect physical properties were also examined, but complete test results are not given here. The amount of Nitrazole-CF in the polymerization recipe had no effect in the range 0.02 to 0.2 part. An increase in the Mooney plasticity of the polymer resulted in higher tensile strength and better hysteresis properties. Optimum properties occurred at 60 per cent conversion; higher values gave poor hystersis and cut growth resistance.

LABORATORY INVESTIGATION OF 41° F DIAZO POLYMERIZATION

As the initial step in the 41° F program, two copolymers (70/30 butadiene-styrene) were made at this temperature with Nitrazole-CF initiation and potassium ferricyanide (0.2 part) to accelerate the rate of polymerization. Although with this recipe about 70 to 100 hours were required for 60 per cent conversion, sufficient copolymer to permit evaluation was made. The physical properties of these copolymers cured in standard tread vulcanizates are presented in Table IV. The data indicate that both Nitrazole polymers have considerably higher tensile strength than either the GR-S control polymerized at 122° F or the GR-S-100 control (X611) polymerized at 41° F.

Further laboratory investigation of low-temperature polymerization with diazo initiation was carried on in two general directions, evaluation of diazo compounds other than Nitrazole-CF, and examination of a number of standard redox activators with Nitrazole-CF. No initiatior was found which gave faster rates than Nitrazole-CF, and the best activators were iron pyrophosphate and iron Sequestrene. A maximum conversion rate of 2 per cent per hour was attained.

PILOT PLANT POLYMERIZATIONS

Long cycle at 122° F.—A fairly large number of pilot-plant runs have been made, using Nitrazole CF initiation, in batches ranging from 5 up to 500 gallons. Preliminary tests were made in 20-gallon autoclaves with the recipe containing

4 parts of soap flakes as emulsifier. Results were similar to those obtained in laboratory bottle runs, although the reaction cycles may have been somewhat shorter.

In an effort to improve cut growth resistance, Dresinate-731 (Hercules Powder Co.) was used in the recipe; this led to much slower runs and higher Nitrazole-CF requirements. The recipe with 4 parts of Dresinate-731 and 0.075 part of Nitrazole-CF initially (plus 0.025 part added incrementwise) was run in the 500-gallon autoclaves to obtain experience on a larger scale as well as a batch of polymer sufficient for factory evaluation. Two series of runs were made; the time cycles ranged from 15 to 39 hours to reach 60 per cent conversion.

TABLE IV

PHYSICAL TEST DATA ON 41° F FERRICYANIDE-ACTIVATED NITRAZOLE CF COPOLYMERS 10 AND 11

Polymer	GR-S	10	11	GR-S-100
Preparation temp. (° F)	122	41	41	41
Raw ML/4/212	47	71	49	52
Cpd. ML/4/212	42	61	51	69
Cure, 60 min. at 280° F				
Modulus at 300%	675	950	675	1425
Tensile strength	3175	4825	4325	3750
Elongation	720	650	740	660
Ring tensile strength at 212° F	900	875	1025	—
Rebound (%)				
72° F	46	47	47	47
212° F	55	65	61	61
Dynamic modulus at 100° C (lb./sq. inch)	182	214	191	235
Internal friction at 100° C (kilopoises)	5.3	4.6	5.0	8.1
3-lb. penetrometer				
Cold	43	35	37	45
Hot	72	50	60	55
Deflection (%)	21.3	15.3	16.7	20.0
Operation temp. (° F)	263	247	253	273
Young's modulus (° C) at 10,000 lb./sq. inch	−45	−41	−42	−46
Aged cut growth, 4 days at 212° F, 0.01 inch/hour	825	843	858	171

In some cases, an increment of Nitrazole-CF was required to keep the charges from "dying out". The two batches of polymer obtained, D332-8 and D346-51, were designated as "long cycle", and were used in the tire tests described later in this report. Polymerization data are shown in Table V.

Short cycle at 122° F.—In view of the impractical nature of slow reactions, further study to shorten the time of polymerization was conducted in the 5-gallon reactors. The logical emulsifier appeared to be a blend of Dresinate-731 and soap flakes. With 4.5 parts of total emulsifier, either a 50/50 or 65/35 blend of Dresinate 731-soap flakes was suitable, while a 75/25 blend resulted in slow reactions. Nitrazole-CF was utilized at the 0.12–0.15 level for best results. The recipe with 4.5 parts of a 65/35 blend of Dresinate-731/soap flakes and 0.15 part of Nitrazole-CF has been designated as the "short cycle" recipe,

TABLE V

PILOT-PLANT RUNS ON 70/30 BUTADIENE-STYRENE
(Nitrazole-CF, at 122° F, in 500-gallon reactor)

Run no.	Time (hours)	Conversion (%)	ML4
Long cycle recipe: water 180, NaOH 0.3, Nitrazole-CF 0.1, Dresinate-731 4.0, BD/S 70/30, MTM variable			
D346	14.8	60	65
D347	39.5	59	71
D348	19.7	60	42
D349	18.5	61	51
D350	23.3	58	58
D351	19.8	61	69
	Av. 23		
D332	23	58	69
D333	20.8	62	57
D334	19.3	60	52
D335	33	58	58
D336	24.7	60	60
D337	34	54	61
D338	19.4	60	70
	Av. 25		
Short-cycle recipe: water 180, NaOH 0.3, Nitrazole-CF 0.15, Dresinate-731 2.9, soap flakes 1.6, MTM variable			
D352	10.25	60	66
D353	13.25	59	77
D354	14.25	60	57
D357	10.0	60	41
D358	17.5	60	57
	Av. 13		

TABLE VI

PILOT-PLANT POLYMERIZATIONS OF 70/30 BUTADIENE-STYRENE AT 41° F IN NITRAZOLE-CF

Run no.	Time (hours)	Modifier	Conversion (%)	ML4
KORR soap with ferricyanide (Redsol) activation				
		MTM		
B1084	80	0.17	59	71
B1087	54	0.20	58	65
B1093	80	0.23	52	48
B1103	89	0.24	54	42
KORR soap with ferrous pyrophosphate activation				
		Sulfole B-8		
B1127	19	0.21	58	38
B1131	26	0.18	60	58
B1133	52	0.18	58	57
Mixed soap[a] with ferrous pyrophosphate activation				
		Sulfole B-8		
B1132	40	0.18	60	62
B1134	37	0.18	53	48

[a] 65/35, Dresinate 731-NaORR.

since 60 per cent conversion is reached in 10 to 14 hours. In contrast, 4 parts of Dresinate-8731 and 0.1 part of Nitrazole-CF are used in the long cycle recipe to give 60 per cent conversion in 23 to 25 hours.

On the basis of the 5-gallon trials of more rapid recipes, polymerizations were carried out in 20- and 500-gallon autocalves to provide increased amounts of polymer for half-and-half tread tests, and later, factory evaluations. The 65/35 Dresinate 731-soap flakes emulsifier system with 0.15 part of Nitrazole-CF was used in all these trials (see Table V).

TABLE VII

FRACTIONATION AND MOLECULAR WEIGHT DATA FOR 122° F, NITRAZOLE-CF POLYBUTADIENE 544

Polymer fraction	Wt. (grams)	% of purified polymer	Intrinsic viscosity	Osmotic mol wt. $\times 10^{-3}$
Whole			2.77	
1	2.22	9.0		
2	2.44	9.9		
3	0.8	3.2		
4	1.59	6.5	5.32	780
5	2.95	11.9	4.35	
6	3.68	14.9	2.67	326
7	2.67	10.8	1.85	177
8	2.82	11.4	1.50	
9	2.62	10.6	1.06	73
10	1.29	5.3		
Unprecipitated	1.59	6.5		

41° F pilot plant runs.—Early pilot-plant polymerizations at 41° F were slow, as at the time these runs were made, the most effective activator known was potassium ferricyanide. The emulsifier was a potassium fatty acid soap (5.0 parts), and 0.20 part of Redsol was used to activate the 0.15 part of Nitrazole. Later runs utilized a ferrous pyrophosphate activator, and in one case a 19-hour time cycle was obtained. However, other runs were very erratic and considerably more study is needed. Results are given in Table VI.

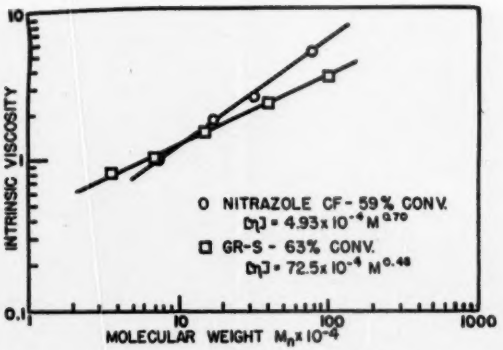


FIG. 1.—Intrinsic viscosity-molecular weight relationship for polybutadiene polymerized at 122° F.

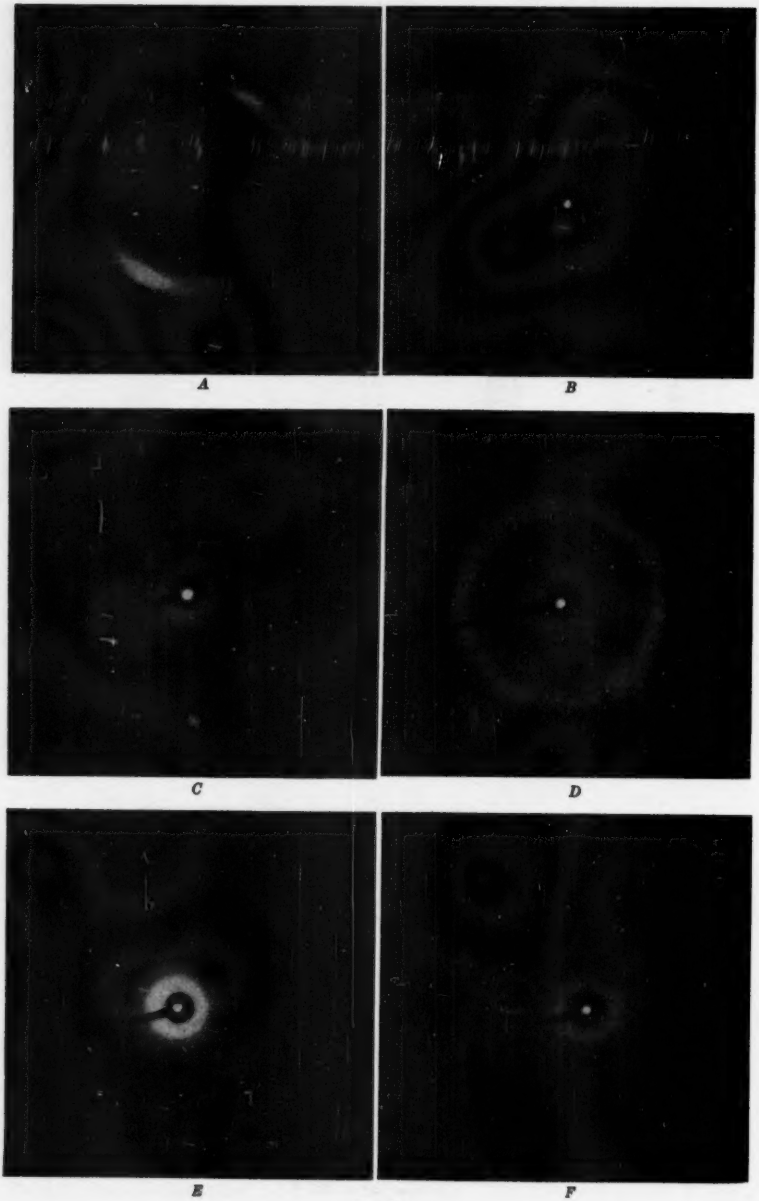


FIG. 2

STRUCTURAL STUDY OF NITRAZOLE-CF POLYMER

Macrostructure.—In an effort to explain the improved properties exhibited by the Nitrazole CF-initiated polymer compared to GR-S made at the same temperature, a number of structural studies were made. To simplify the interpretation of the results, the first tests were carried out on polybutadiene prepared in the systems under study.

Polymer 544, prepared at 122° F in the standard recipe with 0.05 part of Nitrazole-CF and carried to 59 per cent conversion and a Williams plasticity of 3.66, was fractionated into the 10 fractions shown in Table VII. Intrinsic

TABLE VIII

MOLECULAR WEIGHT EXPONENTS OF POLYBUTADIENES

Polymerization system	° F	Conversion (%)	Mol. wt. exponent
Persulfate	122	63	0.45
Redox	41	64.5	0.55
Redox	−4	65	0.63
Nitrazole-CF, 24.5 hours	122	60	0.61
Nitrazole-CF, 13 hours	122	59	0.70

viscosity and osmotic molecular weight values were determined on enough of the fractions to establish the relationship, $[n] = 4.93 \times 10^{-4} M^{0.70}$ (Figure 1). Comparison of the molecular weight exponent of 0.7 with the value of 0.45 obtained on polybutadiene produced in the GR-S system at 122° F indicates that the polymer chain produced in the Nitrazole-CF system is more extended in solution and less cross-linked. In this respect the Nitrazole-CF polymer appears preferable to polybutadiene prepared at a comparable conversion in a redox system at −4° F. Such a polymer[6] has a molecular weight exponent of

TABLE IX

MOLECULAR-WEIGHT DISTRIBUTION OF BUTADIENE-STYRENE COPOLYMERS

Polymer	Feature of polymers	Acetone extract	Per cent polymer in each [η] range						
			0–1	1–2	2–3	3–4	4–5	5–6	Over 6
X630	GR-S	5.0	28.1	21.6	11.1	12.4	16.1	10.7	
B851	Nitrazole long cycle (20 gal.)	9.7	16.0	23.4	14.2	8.9	7.1	9.7	11.0
D332–38	Long cycle (500 gal.)	9.0	20.5	26.2	14.0	9.3	10.0	10.9	
D346–51	Long cycle (3000 lb. lot)	9.5	15.7	29.1	13.8	10.1	11.3	10.3	
B1050	Nitrazole short cycle	9.4	17.4	25.2	14.5	9.4	8.9	14.0	1.2
D352–58	Nitrazole short cycle (3000-lb. lot)	9.4	17.9	24.6	18.4	11.4	10.4	7.4	
X679	Factory production	9.4	17.6	23.8	9.4	11.5	14.4	10.9	3.0
1AR11	Lab. 41° F Nitrazole	14.0	7.1	26.6	20.5	15.3	7.7	8.8	

0.63. The values for the molecular weight exponent of butadiene polymerized in various systems are listed in Table VIII. The lowered exponent obtained by increase of the polymerization time in the Nitrazole system is also of interest because it is consistent with the thought that cross-linking would increase as the time of reaction was lengthened. The correlation of increased cross-linking with longer polymerization cycle may also be significant in explanation of the greater tread-cracking of tires made from long-cycle Nitrazole copolymer.

FIG. 2.—X-ray diffraction patterns of nitrazole CF-initiated copolymers with cold rubber and GR-S controls, showing degree of order.

A. 1AR11. Nitrazole-CF, 41° F. Elongated 500% at −55° C. Strong order
B. B1051–54–58. Nitrazole-CF, 86° F. Elongated 480% at −55° C. Medium order
C. B1050–52–53. Nitrazole-CF, 122° F. Short cycle. Elongated 430% at −55° C. No order
D. D332–338. Nitrazole-CF, 122° F. Long cycle. Elongated 440% at −55° C. No order
E. X599. Low temperature copolymer, 40° F. Elongation 800% at −55° C. Slightly ordered
F. Regular GR-S C361, 122° F. Elongated 490% at −55° C. Slightly ordered

Data on molecular-weight distribution also suggest that an improvement of macrostructure results from copolymerization in the Nitrazole-CF system at 122° F. Comparison of the polymers of Table IX indicates that polymerization in the Nitrazole-CF system at 122° F shifts the distribution toward polymer of higher molecular weight in the case of butadiene-styrene copolymers. A number average molecular weight of 158,000 obtained on the 122° F Nitrazole whole polymer (short cycle D352-58) also indicates an improvement over GR-S, which has a molecular weight of 110,000. In addition to the implication that performance of the 122° F Nitrazole CF copolymer would be better than that of GR-S, the shift in distribution suggests that use of the Nitrazole-CF has altered the relative rates of initiation and termination. The decrease in branching and cross-linking could also be partly responsible for a shift to higher viscosity in the results on molecular-weight distribution. The mechanism of initiation by Nitrazole-CF is being investigated further.

The molecular-weight distribution of a copolymer made in the laboratory at 41° F in the Nitrazole system (1AR11) indicates that the reduction of polymerization temperature has resulted in a further decrease in the amount of low molecular-weight material (Table IX).

Microstructure.—Four Nitrazole copolymers of butadiene-styrene and two controls were studied by the x-ray diffraction method under two conditions:

TABLE X

INFRARED ANALYSES OF NITRAZOLE BUTADIENE-STYRENE COPOLYMERS

Polymer	° F	*cis*-1,4 (%)	*trans*-1,4 (%)	1,2 (%)	Styrene (%)
X599	41	7.9	59.2	7.5	25.4
1AR11	41	7.6	57.3	7.9	27.2
B1051–54–58	86	9.5	53.1	9.1	28.3
B1050–52–53	122	11.7	51.1	9.8	27.4
GR-S	122	12.5	51.2	9.7	26.4

(1) in the extended state at −55° C; and (2) in the relaxed state at 25° C. Considerable order (molecular regularity) was found for the 41° F Nitrazole CF polymer 1AR11; a lesser amount was found in the 86° F Nitrazole-CF copolymer 1051-4-8, but none was found for the 122° F Nitrazole CF copolymers B1050-2-3 and D332-8. Only a very slight amount of order was found in the 41° F cold rubber control, X599, and it is doubtful whether there is any order in the regular GR-S control C361 (122° F). Comparing 1AR11 (41° F) with X599 (41° F), it may be concluded that polymerization at low temperatures is not the only factor that enhances ordering and that the Nitrazole system is a contributing factor. X-ray diagrams (polymer elongated at −55° C) from which the above conclusions were reached are shown in Figure 2.

The infrared spectra of a number of Nitrazole copolymers and one LTP copolymer (butadiene-styrene) were obtained with a Beckman IR2 spectrophotometer, using films cast on rock salt plates from carbon disulfide solutions. In general, the spectra of all the Nitrazole polymers were very similar to the spectra of the control polymers if prepared at the same temperature. Slight differences in 41° F Nitrazole polymer appear in the bands due to C=C (near 6 microns) and in the CH_2 bands (near 7 microns). The amounts of *cis*- and *trans*-1,4-configuration and 1,2-addition, as well as the amount of styrene in terms of per cent by weight, are included in Table X.

TABLE XI

SUMMARY OF FLEET TEST RESULTS ON NITRAZOLE-CF POLYMERS IN TREADS

(122° F, normal Mooney polymers, O and X = control and experimental halves of tread)

Test no.	R.F.C. project no.	Polymer no.	Feature	Carbon black	No. of tires	Size	Final[a] mileage	Wear rating	Cracking	Cut growth (inches)
1	120CC	O GR-S-AC	70/30-BD/ST at 122° F	EPC	2	6.00–16	17,800	100	None	1
		X B659	Nitr.-CF, 70/30-BD/ST at 122° F, soap flakes, 23-hr. cycle					105	None	1
2	120DJ	O X599	LTP, 70/30-BD/ST at 41° F, Dresinate-214	HAF	2	8.00–15	24,617	100	None	0
		X B851-2 X B851-3	Nitr.-CF, 70/30-BD/ST at 122° F, Dresinate-731, 23-hr. cycle					99	None	2
3	[b]	O X611	LTP, 75/25-BD/ST at 41° F, Dresinate-214	HAF	2	8.00–15	16,000	100	Mod.	7.2
		X D332-8	Nitr.-CF, 70/30-BD/ST at 122° F, Dresinate-731, 23-hr. cycle					100	Mod.	19.7
4	[b]	O D332-8	Nitr.-CF, 70/30-BD/ST at 122° F, Dresinate-731, 23-hr. cycle	HAF	2	8.00–15	16,000	100	Mod.	12.4
		X B1050	Nitr.-CF, 70/30-BD/ST at 122° F, Dresinate-731/NaORR, 14-hr. cycle					103	Sl.	4.4
5	204A	X611	LTP, 75/25-BD/ST at 41° F,	HAF	4	8.00–15	20,754	100	None	1.4
	204B	D346-51	Nitr.-CF, 23 hr. at 122° F. Dresinate-731					88	None	2.1
									None	4.6
	204C	D352-8	Nitr.-CF, 14 hr. at 122° F, Dresinate-731/NaORR, 70/30-BD/ST					89		
6	[b]	X611	Same as 5	HAF	40	6.70–15	17,000	100	None	—
		D346-51			40	6.70–15	17,000	99	None	—
		D352-8			40	6.70–15	17,000	101	None	—
7	[b]	O X611	LTP, 75/25-BD/ST at 41° F,	HAF	2	8.00–15	16,000	100	None	0.5
		X D352-8	Nitr.-CF, 14 hr. at 122° F, Dresinate-731/NaORR, 70/30-BD/ST					91	None	1.0
8	[b]	O X611	Same as 7	HAF	2	8.00–15	16,000	100	None	0.6
		X D352-8	Treads lab.-pressed for 7 and factory-tubed for 8					101	None	1.6
9	[b]	O X611	LTP, 75/25-BD/ST at 41° F, Dresinate-214	HAF	4	6.70–15	16,000	100		0.8
		X X679	Nitr.-CF, 14 hr. at 122° F, 70/30-BD/ST, Dresinate-731/NaORR					118		2.0

[a] Final mileage records mileage used for rating tread wear based on nonskid depth, and does not indicate worn-out mileage of tire. [b] Tests run on Firestone test fleet.

FLEET TESTS OF 122° F NITRAZOLE-CF POLYMER

A summary of fleet-test results on tires with tread stocks utilizing 122° F Nitrazole-CF polymer is presented in Table XI. A brief summary of tread stock physical properties, itemized by test number, is given in Table XII.

The initial test on Nitrazole-CF polymer was made with EPC black and with GR-S-AC as a control. A wear rating of 105 per cent of GR-S-AC was obtained. This has been the only test comparing GR-S-AC and Nitrazole-CF polymer. The other eight tests listed in Table XI compare Nitrazole-CF polymer to X611 in HAF black stocks. Wear ratings range from 118 for X679 (factory batch of Nitrazole-CF polymer) in test 9 to the 88 and 89 obtained in

TABLE XII

LABORATORY PHYSICAL PROPERTIES OF NITRAZOLE AND CONTROL TREAD STOCKS

Test no.	Polymer	Min./ 280° F	300% modulus (lb./sq. inch)	Tensile (lb./sq. inch)	Elongation (%)	Aged tensile[a] (lb./sq., inch)	Oper. temp. (°F)	Internal friction kps. at (100°C.)	Cut growth (0.01 inch/ hour)[b]
1	O GR-S-AC	80	750	3300	700	2350	287	6.3	843
	X B659	80	850	3675	660	2700	261	5.6	900
2	O X599	60	1650	3850	620	2950	276	7.0	250
	X 851–2–3	60	1650	3325	540	2850	286	6.7	269
3	O X611	60	1600	3275	520	3000	268	7.6	314
	X D332-8	60	1825	3200	460	3125	264	7.8	590
4	O D332–8	60	1725	3325	510	2700	304	7.1	486
	X B1050–2–3	60	1425	3375	570	2975	302	7.6	529
5 and 6	X611[c]	60	1850	3750	530	3250	267	7.0	204
	D346–51[c]	60	1200	2600	550	2975	315	7.9	231
	D352–8[c]	60	1475	2950	510	2900	280	6.6	160
7	O X611	60	1800	3575	540	3050	255	6.3	272
	X D352–8	60	1975	3250	450	2875	249	6.1	361
8	O X611	60	1975	3700	490	3350	259	6.2	262
	X D352–8	60	2375	3475	360	2800	247	5.6	516
9	O X611	60	—	—	—	—	—	—	—
	X X679	60	3000	4150	400	—	—	—	—

[a] Aged 2 days at 212° F in oven.
[b] Aged 5 hours at 260° F in air bomb.
[c] Whole treads.

test 5. The same stocks when run in 6.70-15 tires in test 6 gave wear ratings of 99 and 101, respectively. Treads for both of these tests were tubed in the factory from the same stocks, and it is felt that the test results represent the variation possible under different test conditions, and that the high temperatures developed in factory mixing affected the ultimate tread wear. Therefore, tests 7 and 8 were run to compare laboratory pressed treads with factory tubed treads. In this case, the factory treads gave the best results.

The variability of results obtained in road tests to this point in the program, as well as the high tubing temperature and other indications of poor processability which were encountered, suggested instability of the polymer during factory processing. Therefore a program was set up to study the stabilizing

effect of various compounds on X679 (factory batch of 122° F Nitrazole-CF polymer) at high temperatures in a laboratory Banbury mixer. The stabilizing agent at the level of 0.5 part per hundred of rubber was introduced on a cool mill and the stabilized polymer was then massed in a 350° F Banbury for 6 and 9 minutes. The effectiveness of the various materials was measured by Mooney plasticity and gel determinations on the various samples before and after the Banbury treatment. The most effective stabilizer for X679 was found to be Santovar-O (2,5-di-*tert*-butylhydroquinone) (Table XIII). The results indicated that an increase of gel content, but not Mooney plasticity, occurs in this polymer during high-temperature processing. The sodium dimethyldithiocarbamate and sulfur stopping agent and phenyl-2-naphthylamine (PBNA) antioxidant have been shown to protect the polymer during processing at the synthetic plant, but they are apparently inadequate at the +300° F temperatures encountered in the tire factory. Santovar-O when added to the dry rubber before compounding (0.5 part per hundred of rubber) increased stability. (Subsequent studies have shown that the requirements for the addition of Santovar-O to Nitrazole-CF polymer latex were higher because apparently not all of the material added was available for stabilizing.)

TABLE XIII

EVALUATION OF STABILIZERS FOR X679 (122° F NITRAZOLE-CF POLYMER)

(High temperature Banbury massing)

	Original		6 min. at 350° F		Original		9 min. at 350° F	
Test material	ML/4/212	Gel(%)	ML/4/212	Gel(%)	ML/4/212	Gel(%)	ML/4/212	Gel(%)
Santovar-O	41	0.5	29	0.9	41	1.1	28.5	1.5
Hydroquinone	41	0.5	31.5	0.8	46	1.6	34	17.5
Antioxidant-2246	44	1.3	35.5	22.0	42	1.3	38.5	27.0
Control (blank)	43	1.1	56	33.0	42	0.9	49	35.9
RPA No. 5	42.5	1.5	42.5	35.5	39	0.9	37	45.5
Quinone	45	1.1	54	37.1	41.5	1.1	55.5	42.0
Mercaptobenzothiazole	40.5	1.2	42	43.7	42	4.3	34	47.7
2-Methyl-5-butylphenol + acetaldehyde	43	1.3	51.5	42.0	40.5	1.1	37.5	45.2

It was concluded that the addition of 0.5 part of Santovar-O to the Banbury batch immediately after charging the polymer was a suitable method of application for polymer already prepared. This technique was utilized in factory runs and resulted in lower tubing temperatures and smoother treads. Some of the variation in wear results may be related to accelerator changes dictated by the tubing temperatures. For example, in test 9 (Table XI), Santovar-O (0.5 part) was added during factory mixing and normal tread tubing temperatures were realized. This permitted a somewhat higher accelerator level than would otherwise have been possible.

FLEET TESTS OF NITRAZOLE-CF POLYMERS MADE AT REDUCED TEMPERATURES

Table XIV lists the results of tire tread tests on Nitrazole-CF polymers made at 86° and 41° F. The wear ratings obtained show these particular Nitrazole-CF polymers made at reduced temperatures to be inferior in abrasion resistance to both X611 and 122° F Nitrazole-CF polymer. Physical properties of the tread stocks are presented in Table XV.

TABLE XIV

SUMMARY OF FLEET TEST RESULTS ON NITRAZOLE-CF POLYMERS IN TIRES

(Tire tests run on Firestone fleet. Polymers made at reduced temperature. 0 and X = control and experimental halves of treads)

Test no.	Polymer no.	Feature	Carbon black	No. of tires	Size	Final mileage	Wear rating	Cracking	Cut growth (inches)
10	O X611	LTP, 75/25-BD/ST at 41° F, Dresinate-214	HAF	2	8.00–15	11,000	100	None	2.2
	X B1084–103	Nitr.-CF, at 41° F, 70/30-BD/ST, KORR soap, 80-hr. cycle					75	None	0.4
11	O D352–8	Nitr.-CF, 14 hr. at 122° F, 70/30-BD/ST Dresinate-731/NaORR	HAF	2	8.00–15	11,000	100	None	2.6
	X B1084–103						83	None	0.4
12	O X611		HAF	2	8.00–15	8,000 and 12,000	100	None	1.0
	X B1132–4	Nitr.-CF at 41° F, 70/30-BD/ST, Dresinate-731/NaORR, 40-hr. cycle					104 and 93	None	1.2
13	O X611		HAF	2	8.00–15	8,000 and 12,000	100	None	0.3
	X B131	Nitr.-CF at 41° F, 70/30 BD/ST KORR, 26-hr. cycle					77–89	None	0.2

TABLE XV

LABORATORY PHYSICAL PROPERTIES OF LOW-TEMPERATURE NITRAZOLE AND CONTROL TREAD STOCKS

Test no.	Polymer	Min./ 280° F	300% modulus (lb./sq. inch)	Tensile (lb./sq. inch)	Elongation (%)	Aged tensile[a], (lb./sq. inch)	Operating temp. (° F)	Internal friction (kps. at 100° C)	Cut growth (0.01 inch/ hr.[b])
10	O X611	60	2050	4025	540	3300	262	6.6	144
	X B1084-103	60	1800	3750	600	3250	282	6.9	336
11	O D352-8	60	1325	3100	580	3075	304	7.6	238
	X B1084-103	60	1650	3600	570	3075	288	7.1	544
12	O X611	60	1975	3600	510	3375	273	7.1	162
	X B1132-4	60	2825	3500	360	3300	238	5.9	510
13	O X611	60	1975	3600	510	3375	273	7.1	162
	X B1131	60	2325	3525	420	3350	260	6.4	900

[a] Aged 2 days at 212° F in oven.
[b] Aged 5 hours at 260° F in air bomb.

ACKNOWLEDGMENT

The authors wish to thank the following collaborators for their assistance on certain sections of this report; R. L. Bebb for suggestions and encouragement; J. W. Ballard for x-ray diffraction studies, and J. L. Binder for infrared spectra.

REFERENCES

[1] Reynolds and Cotton, *Ind. Eng. Chem.* **42**, 1905 (1950).
[2] Buizov, Russian patent 1103 (July 20, 1927); German patent 521,903 (Mar. 12, 1931).
[3] Fryling (to B. F. Goodrich Co.), U. S. patent 2,313,233 (Mar. 9, 1943); Semon and Fryling (to B. F. Goodrich Co.), U. S. patent 2,376,041 (May 15, 1945); Garvey (to B. F. Goodrich Co.), U. S. patent 2,276,963 (May 29, 1945); Walker (to E. I. du Pont de Nemours & Co.), U. S. patent 2,382,684 (Aug. 14, 1945); Hunt (to E. I. du Pont de Nemours & Co.), U. S. patent 2,471,959 (May 31, 1949); Marks (to E. I. du Pont de Nemours & Co.), U. S. patent 2,516,064 (July 18, 1950); Robertson, U. S: patents 2,520,338 and 2,520,339 (Aug. 29, 1950).
[4] Pratt, "The Chemistry and Physics of Organic Pigments," John Wiley & Sons, Inc., New York, 1947; Saunders, "Aromatic Diazo Compounds and Their Technical Applications," Edward Arnold, London, 1949.
[5] Hickinbottom, "Reactions of Organic Compounds," Longmans Green & Co., New York, 1948, 2nd Ed., p. 383.
[6] Johnson and Wolfangel, *Ind. Eng. Chem.* **41**, 1580 (1949).

YIELD STRESS IN FROZEN RUBBERS *

J. M. Buist and R. L. Stafford

Rubber Service Laboratory, Dyestuffs Division, Imperial Chemical Industries, Ltd., Hexagon House, Blackley, Manchester, England

INTRODUCTION

During the last war, intensive work was done to devise suitable test methods for studying the physical properties of polymers at low temperatures. A multitude of methods has been used; many were simple extensions of existing methods operated at low temperatures, *e.g.*, stress-strain tests, hardness and permanent set; others were specifically designed to investigate low temperature behavior, *e.g.*, flexibility, brittleness. As data became available from all these tests, it was clear that the low-temperature characteristics of a given polymer could not be classified simply by a single figure or property. Further, the position was complicated by the fact that conditioning and previous history of the sample and the method of cooling the sample influenced the results obtained. These factors, along with the lack of any unique characteristic to describe the low-temperature performance of a rubber article under the wide range of service conditions, led many to ask what were the main important conditions in service. The rubber physicist is, therefore, presented with the same fundamental problem in studying low-temperature characteristics as when studying flex-cracking and abrasion resistance, and there is generally the same lack of accurate service information.

Before considering the effect of service conditions, it may be useful to summarize the general picture of what changes occur in rubberlike polymers when the temperature is lowered. When subjected to low temperatures, natural and synthetic rubbers undergo a progressive change of properties which depends on both time and temperature[1]. For example, as the temperature decreases, they steadily become harder, less flexible, and less elastic; they then pass through a leatherlike stage and finally become brittle and less capable of resisting shock. This general picture might suffice if the rate of change of one physical property corresponded to the rates of change of several other physical properties, but unfortunately this is not so, and therefore the mechanism of the changes involved must be studied more closely.

The three fundamental changes which take place on lowering the temperature are:

(1) Stiffening due to an increase of cohesive forces brought about by restricted molecular movement at the lower temperature.
(2) Crystallization, which is accompanied by a volume change, and which requires time for its development, depending on the polymer structure and on the temperature of storage.
(3) A second-order transition, evidenced by a rapid change of physical properties within a narrow temperature range[2].

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 5, pages 238–254, October 1953.

As both the transition temperature and the temperature for maximum rate of development of crystallization vary widely for different polymers, each polymer must be studied over a wide range of temperature. The results of storage tests at one temperature cannot be used to predict the behavior at any other temperature.

Crystallization in unstretched rubber is thought to be a slow process, and is said to be most rapid at temperatures between −35° and −15° C; at −50° C it has been reported that no crystallization occurs[3]. The latter statement must be accepted with some reserve, however, since as at −50° C the size of the crystallites formed may be so small as to make their detection difficult. Previously it has been thought that, for most practical purposes, crystallization is a secondary effect, but this does not mean that the effects of rate of cooling and of the temperature range favoring crystallization can be overlooked. At the present time, little systematic work has been carried out on the effects of

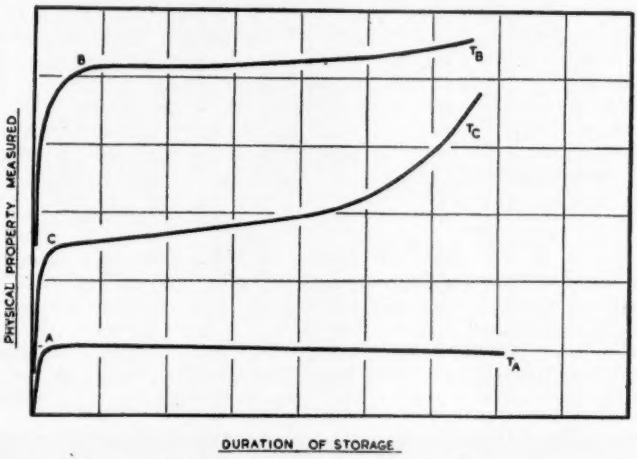


FIG. 1.—Storage tread compounds at −20° C.

prolonged storage at low temperatures, but the data available[4] emphasize the importance of considering fully this factor.

The fact that crystallization is dependent on time emphasizes the importance of carrying out low-temperature tests over a prolonged period. During 1945 and 1947, considerable work was carried out by the I.C.I. Rubber Service Department on the effects of prolonged storage at −20° and −40° C on a wide range of physical properties and over a wide range of natural and synthetic rubber compounds. This work was carried out at the Royal Aircraft Establishment, Farnborough, where facilities are available for housing both the apparatus and the operator in large refrigerators. The results of the work at −20° C have already been published[2] and the combined results at both temperatures are shortly to be published by H. M. Stationery Office[5]. As a result of this work it was quite clear that effects of storage at one temperature cannot be used in predicting behavior at a different temperature, since the time-dependent effects of crystallization vary so markedly with temperature. The

effects of the variation of crystallization with both time and temperature can be summarized as follows (Figure 1).

T_c is the temperature at which crystallization is most rapid. T_a is well above and T_b well below T_c. The points, A, C and B represent the effects of temperature alone on the physical property measured, and are largely explained in terms of the increase of cohesive forces with decreasing temperature common to all polymers. In the case of T_a, no crystallization is assumed to develop, and the magnitude of the physical property remains constant (= A) in time. In the case of T_b, only a very slow development of crystallization occurs, while at T_c a very marked, and rapid change of physical properties can occur with time. It is obvious that short period tests, which determine only the points A, C and B, could be quite useless in estimating behavior in service when prolonged exposure to low temperatures is involved.

During the course of the work at −40° C carried out at Farnborough, a most interesting phenomenon was observed. Extensometer tests were carried out to determine the modulus of natural rubber, GR-S, Neoprene-GN, Perbunan, Thiokol-FA, Vulcaprene-A and polyvinyl chloride. With all the polymers, apart from natural rubber and GR-S, cold-drawing occurred during the modulus test. In other words, these polymers are far removed from the rubberlike state and on stretching reveal a definite yield stress. This phenomenon has not previously been reported in the literature in connection with elastomers. The remainder of this paper deals with a subsequent investigation of this yield phenomenon.

INVESTIGATION OF THE YIELD STRESS OF FROZEN RUBBERS

It was decided to investigate further the remarkable phenomenon of a *yield stress* revealed in the above work on rubbers stored at −40° C and subsequently stretched. The phenomenon is very marked in the case of Neoprene-GN, and can be demonstrated by simple hand tests on thin sheets. After storage at −40° C, the Neoprene-GN gum compound is frozen hard, but its appearance is unchanged. On applying a stretching force, the test-piece resists deformation (at −40° C) until white spots appear in the rubber. At

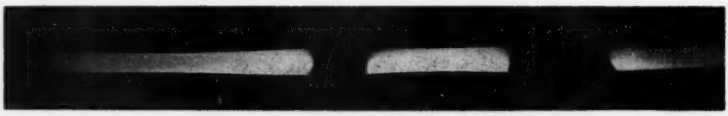


FIG. 2.—Neoprene-GN at −40° C.
Test-piece yielding under tension.

this point the yield of the test-piece can definitely be felt, and the white areas spread along the test-piece accompanied by necking (Figure 2).

On removing the stretching force, the whitish coloration remains, and only slowly disappears on warming the specimen to room temperature. Even after several hours at room temperature, subsequent stretching at this temperature causes a faint reappearance of the white coloration in those places at which it appeared on stretching while frozen at −40° C.

In view of the quite definite effects shown by Neoprene-GN, the following investigations were limited to Neoprene-GN and natural-rubber gum compounds. Gum compounds were used to avoid any effects of filler structure and to facilitate x-ray measurements.

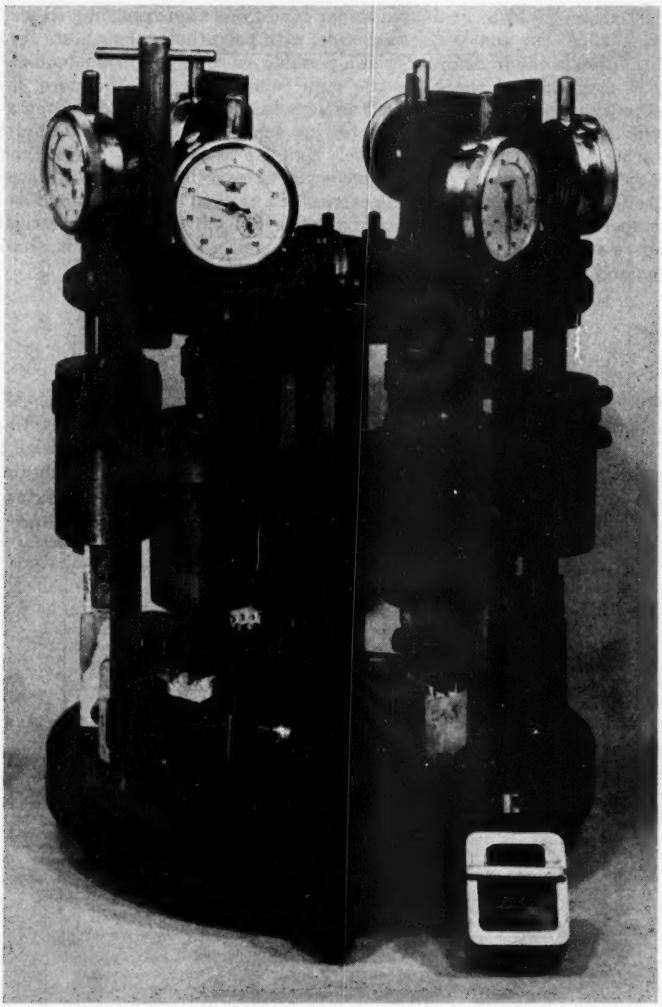


FIG. 3.—Modified ICI shear-creep apparatus.

Although deformation in tension to high elongations first revealed the yield-stress effect, such a mode of deformation has little practical significance. The present investigations were, therefore, made on double-sandwich shear test-pieces of the engine-mounting type. It was anticipated that the relative effects of yield on the shear deformation of such a test-piece would be much more difficult to detect, but it is important that the practical consequences of

such an effect should be evaluated under conditions approximating to service. The yield effect (by analogy, for example, with polyethylene) suggests crystallite formation in the frozen rubber as a possible cause of the phenomenon. An x-ray investigation of the same two gum compounds was, therefore, made. Of necessity this must be performed on very thin test-pieces. Although x-ray analysis is not very sensitive for detecting small amounts of crystallinity in elastomers, the method is comparatively simple practically, and it was thought that any major changes of crystallinity would at least be revealed qualitatively.

The low-temperature work was carried out at $-40°$ C only, since this was the temperature at which yield was first detected. Obviously the investigation should be extended to a range of temperature and a wide range of elastomers, particularly oil-resistant rubbers.

DEFORMATION IN SHEAR AT $-40°$ C

EXPERIMENTAL

A modified I.C.I. shear creep apparatus was used, in which the shear deformation could be followed continuously on dial micrometers (Figure 3).

Ten per cent nominal compression was applied to the double-sandwich test-pieces, and shear loads of 20, 40 and 60 pounds were applied to the specimens after storage for 4, 16 and 64 hours at $-40 \pm 1°$ C. The whole apparatus was housed in a large refrigerator equipped with a defrosted viewing window. All

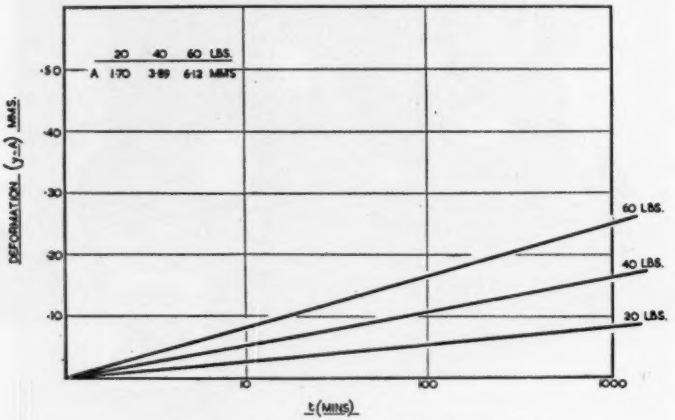


FIG. 4.—Natural rubber. Room temperature (19° C).

moving parts were lubricated with a mixture of dioctyl sebacate and dioctyl adipate. The test-pieces were first conditioned in the apparatus at $-40°$ C for the appropriate period; full shear load was then applied in one minute.

Although only primarily interested in the short-period deformation in this work, total shear-deformation curves to 140 hours were first made at room temperature ($19 \pm 1°$ C) in order to provide reference data for the low-temperature deformation curves.

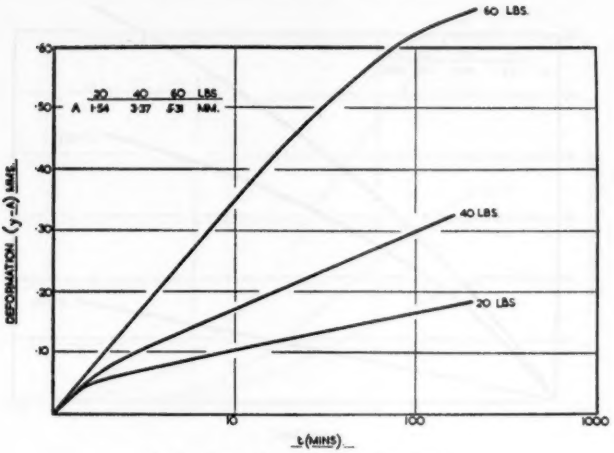


FIG. 5.—Natural rubber. 4 hours −40° C.

Similarly, although only the short-period deformation is envisaged in the yield phenomenon, observations of continued deformation were made for 3–5 hours after first application of full load at −40° C. This period of 3–5 hours is quite arbitrary, and in some cases proved unfortunate in that it did not reveal what is considered to be the complete shear-deformation × time curve. However, one wished to avoid as far as possible the effects of continued storage at

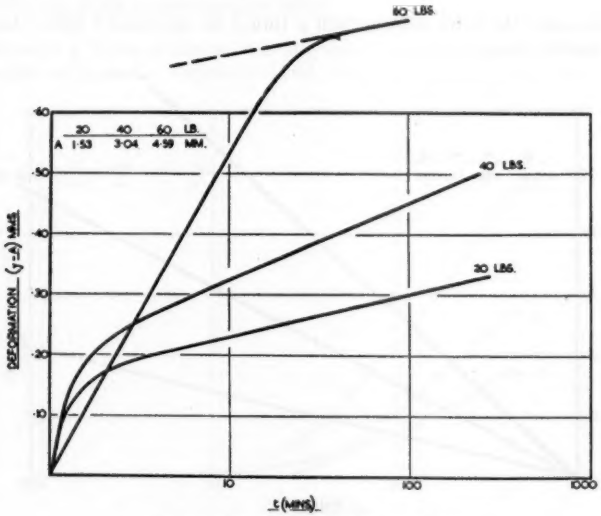


FIG. 6.—Natural rubber. 16 hours −40° C.

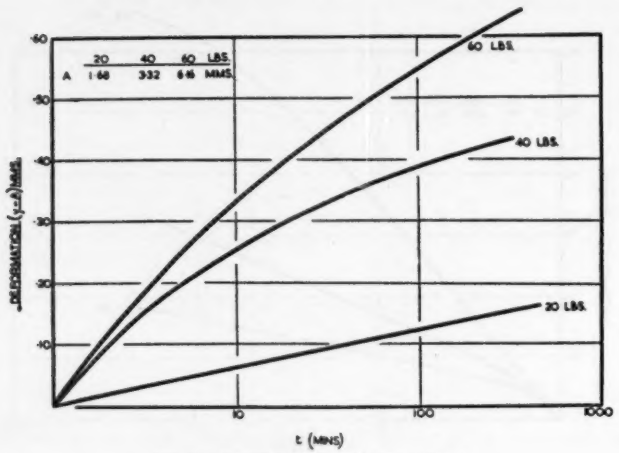


FIG. 7.—Natural rubber. 64 hours −40° C.

−40° C during the course of observations, and a compromise total time had to be fixed beforehand.

No attempt was made to correct for stress-relaxation during observations, but direct reading of the load scale pointer showed that this never exceeded 3–4 per cent of full load in those curves where it could be observed at all.

TREATMENT OF RESULTS

In all cases, the total deformation y (mm.) at any time t (min.) has been plotted against $\log_{10} t$.

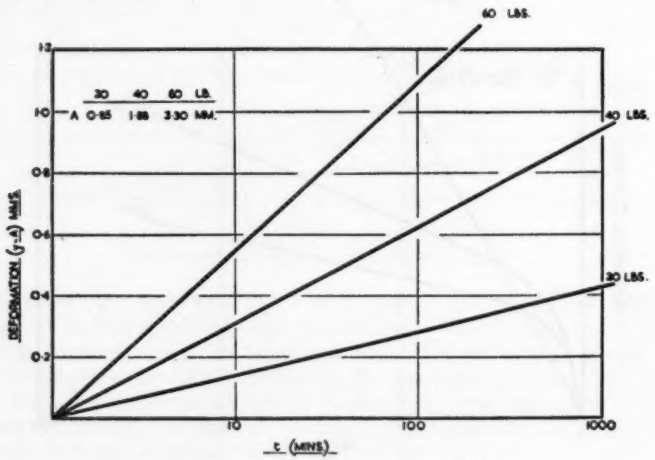


FIG. 8.—Neoprene-GN. Room temperature (19° C).

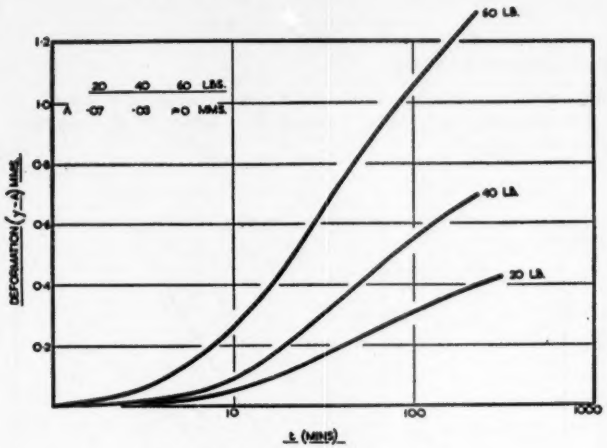


FIG. 9.—Neoprene-GN. 4 hours −40° C.

Since in nearly all cases the application of full load was made in 1 minute, this time has been taken as the zero for subsequent deformation under load.

For a linear relation:

$$(y - A) = B \log_{10} t \quad (t \geqslant 1)$$

where A = 1-minute deformation (mm.)
B = log slope in appropriate units.

For nonlinear $y \times \log_{10} t$ curves, the tangential slope at any time is expressed in the same units as B. Figures 4–11 show all the experimental data.

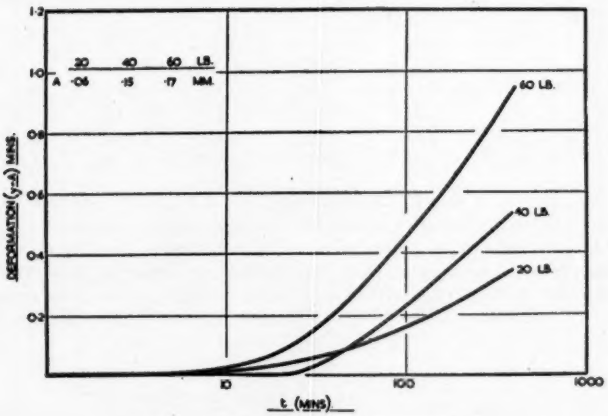


FIG. 10.—Neoprene-GN. 16 hours −40° C.

DISCUSSION OF RESULTS

(*A*) *Room Temperature Curves*

All the curves are linear to 140 hours within experimental error. Assuming $y = A + B \log_{10} t$ ($t \geq 1$), Table 1 shows the values of the constants (A in mm., B in mm./$\log_{10} t$).

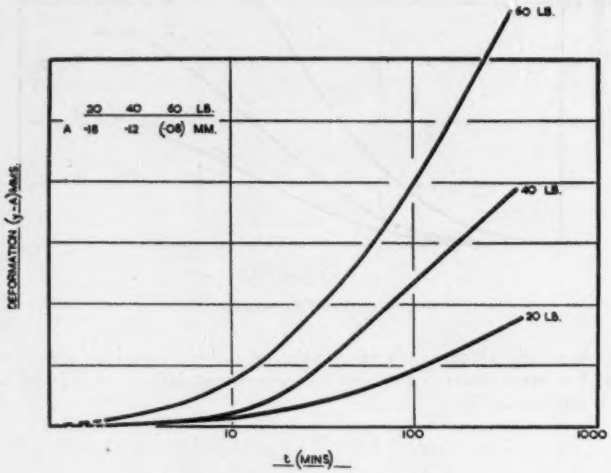


FIG. 11.—Neoprene-GN. 64 hours −40° C.

The ratios of the shear stresses are 1:2:3; the values of the corresponding A ratios and B ratios are shown in Table 2.

In the case of natural rubber, the log slope is proportional to the applied stress under the range investigated, but Neoprene-GN shows progressive departure from this proportionality.

TABLE 1

Load (lb.)	Natural rubber			Neoprene-GN		
	20	40	60	20	40	60
A	1.70	3.89	6.12	0.85	1.88	3.30
B	.027	.053	.083	.140	.313	.550

As regards the 1-minute deformation ($y_1 = A$), both rubbers show departures from proportional dependence on applied stress. This may be due to accumulated creep during application of the load within the first minute.

From Table 1 it is seen that the initial room-temperature stiffness of Neoprene-GN is approximately twice that of natural rubber, the subsequent log rate of deformation being about 5–7 times as great as that of natural rubber.

TABLE 2

	A Ratios	B Ratios
Natural rubber	1 : 2.3 : 3.6	1 : 2 : 3
Neoprene-GN	1 : 2.2 : 3.9	1 : 2.2 : 3.9

(B) Initial (1 minute) Stiffness after Storage at −40° C

Since all the test-pieces are of nominally the same dimensions, the value of A (the 1-minute deformation) is a measure of 1/shear stiffness. Table 3 shows the values of A after 3 periods of storage at −40° C.

The room temperature values are given again for reference.

TABLE 3

A (INITIAL DEFORMATION—MM.)

Compound		Natural rubber			Neoprene-GN		
Applied load (lb.)		20	40	60	20	40	60
Temp. (° C)	Storage time (hrs.)						
19	—	1.70	3.89	6.12	0.85	1.88	3.30
−40	4	1.54	3.37	5.31	0.07	0.03	0
−40	16	1.53	3.04	4.59	0.06	0.15	0.17
−40	64	1.68	3.32	6.16	0.18	0.12	(0.08)*

* Value not reliable. The first reading was made at 2 minutes, and the value given above is an attempted extrapolation to 1 minute.

The following points are shown by the above table.

(1) Stiffening of the rubbers at −40° C is shown in all cases after 4 hours' storage. In the case of natural rubber, this amounts to a 10–20 per cent increase in initial modulus; in the case of Neoprene-GN, to 1000 per cent or more. Little weight can be placed on the initial deflections of Neoprene-GN measured at −40° C, since these are very small in most cases, but the poor low-temperature resistance of this rubber is very clearly shown.

(2) The most outstanding result is that, after continued storage at −40° C, the 1-minute deformation begins to increase. In the case of natural rubber, this initial deformation can become equal to, and even exceed, the corresponding deformation at room temperature at the highest shearing stress.

The above result cannot be due to the effect of temperature on the relaxation process, since the deformation changes with time of storage at −40° C. The deformation decreases slightly from 4–16 hours' storage in all cases, but between 16 and 64 hours the deformation increases. This effect must, therefore, be due to continued storage of the rubber at −40° C, and is shown above as an apparent softening or yield on the application of shear stress. A reasonable hypothesis is that the effect is due to crystallite formation in the natural rubber at −40° C.

In the case of Neoprene-GN, although the initial deformation shows a tendency to increase with storage time it still remains very much smaller than the room temperature figure. Under the conditions of shear deformation used, the very large temperature stiffening of Neoprene-GN tends to mask any yield effects produced by continued storage at −40° C.

(C) Continued Shear Deformation after Storage at −40° C

After storage at −40° C, the shear deformation (y) against $\log_{10}t$ curves are no longer linear, as they are at room temperature.

In the case of natural rubber, the $\log_{10}$ rate of deformation is high initially, falling to a nearly constant value. In the case of Neoprene-GN the curves are S-shaped.

There is some evidence in the experimental curve that the log rate eventually approaches the room temperature rate at the corresponding applied stress. The rate may, of course, continue to fall below that of the room temperature value if observations were continued long enough, but in the present investigation it was desired to reduce as much as possible the time effect of continued storage during the observations.

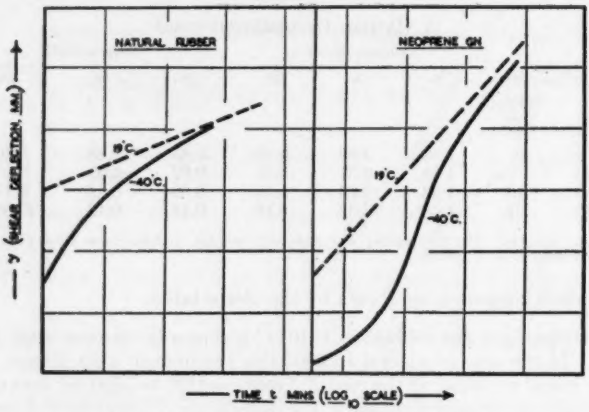


FIG. 12.—Characteristic shear deformation curves.

In the absence of yield effects, the diagrams in Figure 12 appear to represent fairly the shear deformation characteristics at −40° C of the two rubbers.

Table 4 shows the value of B (log rate of shear deformation) determined from the experimental curves. In the case of natural rubber, B is the quasi-linear value after the initial high rate. In the case of Neoprene-GN, B is the

TABLE 4

VALUES OF B

Compound		Natural rubber			Neoprene-GN		
Applied load (lb.)		20	40	60	20	40	60
Temp. (° C)	Storage time (hrs.)						
19	—	.027	.053	.083	.140	.313	.550
−40	4	.063	.130	.340→.130	.270	.55	.92
−40	16	.070	.125	.520→.08	.270	.53	.87
−40	64	.062	.130→.067	.72 →.16	.260	.57	.99

inflexion value of the rate (or the end rate in those cases where the inflexion had not been quite attained). The room temperature values are given again for reference.

The following points emerge from the above data.

(1) After any period of storage from 4–64 hours at −40° C, the rate of deformation in shear is always increased at least in the first hour or two of

deformation. In the case of natural rubber, the increase in log rate is 2–3 fold; in the case of Neoprene-GN, rather less than 2 fold.

(2) In those cases of natural rubber where initial yielding has taken place, the total low-temperature deformation of the loaded shear unit could exceed the corresponding deformation at room temperature. With Neoprene-GN at −40° C under the conditions examined above, the total low-temperature shear deformation is hardly ever likely to exceed the corresponding room-temperature deformation.

Table 5 illustrates this point by showing the total actual shear deformation of the test-pieces 100 minutes after the loading was commenced.

The data above show that a natural rubber shear unit in service at −40° C might fail either by yielding and giving too much deflection, or by stiffening and not giving sufficient deflection. Neoprene-GN is obviously more likely to fail in service by becoming too rigid at low temperature, particularly at temperatures below that at which maximum rate of crystallization occurs.

TABLE 5

TOTAL DEFORMATION (MM.)

Compound		Natural rubber			Neoprene-GN		
Applied load (lb.)		20	40	60	20	40	60
Temp. (° C)	Storage time (hrs.)						
19	—	1.75	4.00	6.29	1.13	2.50	4.39
−40	4	1.71	3.67	5.93	0.39	0.58	1.06
−40	16	1.83	3.49	5.34	0.22	0.38	0.53
−40	64	1.81	3.71	6.71	0.36	0.59	0.87

(3) Further evidence of yielding of natural rubber at −40° C is afforded by the values of B (see Table 4), at 60-lb. shearing load. The initial very high values at this load far exceed the approximate proportional increase with load shown by the room temperature values and the −40° C values at 20- and 40-lb. load. This shows that the effects of continued storage are more clearly revealed the higher the applied shearing stress.

X-RAY DIFFRACTION AT −40° C

EXPERIMENTAL

A small perspex extensometer mounted inside a perspex box was built so that it could be mounted in an *x*-ray camera. A controlled source of boiling liquid nitrogen was attached to the box via Dewar tubes. The temperature of a small rubber test-piece (0.6 cm. wide, 0.07 cm. thick, and 0.8 cm. long between the jaw grips) could be maintained at −40 ± 2° C in this way for long periods.

A small hole in the front of the box covered with defrosted cellophane allowed the emergent diffracted *x*-ray beam to be photographed. The average period of exposure per film was 1 hour.

The rubber test-piece, mounted in the extensometer, was first stored for the appropriate period in a refrigerator at −40° C. The test-piece was then stretched, and the whole box, housed in a Dewar flask at −40° C, transferred to the *x*-ray camera.

EXPERIMENTAL DATA

X-ray exposures were made both at room temperature (21° C) and −40 ± 2° C on stretched and unstretched test-pieces. Table 6 summarizes the conditions of temperature, storage time, and percentage elongation; it applies to both natural rubber and Neoprene-GN.

In the case of the Neoprene-GN, test-pieces at −40° C, the elongations quoted are purely nominal, since all the samples cracked and yielded on initial extension. The degree of actual elongation, and even the significance of this term is, therefore, doubtful.

During the period of *x*-ray exposure (about 1 hour) some permanent set, as judged at room temperature on the relaxed test-piece, occurred; the above elongations are the nominal elongations on first stretching the test-piece.

In addition to the above exposures, tests were made after 16 hours' storage at −40° C, followed by stretching to 200 per cent at −40° C, and then allowing the test-piece to warm up to 21° C before exposing to *x*-rays. The test-piece

TABLE 6

Temperature	Storage time before stretching (hrs.)	Per cent elongations (different test-pieces)
21° C	—	0, 100, 200 and 300
−40° C	4	0, 200
−40° C	64	0, 200 and 300

was then returned to the unstretched state at 21° C and again exposed. The object of this test was to determine if stretching at −40° C produced any persistent effect at room temperature.

No attempt has been made to analyze the *x*-ray photographs quantitatively. The following qualitative description can be given.

DISCUSSION OF RESULTS

(*A*) *Room Temperature*

(1) In the unstretched state, both natural rubber and Neoprene-GN show a central halo typical of an amorphous solid. In addition, natural rubber shows an outer diffuse ring, the origin of which is uncertain; in the most general terms, however, it can be said that the structure of natural rubber is more ordered than that of Neoprene-GN.

(2) On stretching to a nominal 300 per cent extension, the natural-rubber compound showed no sign of orientation crystallization. With Neoprene-GN, an outer diffuse ring appears on stretching, and diffraction spots have appeared by 200 per cent elongation, becoming rather more marked at 300 per cent.

(*B*) *Storage at −40° C*

(1) After storage for 4 and 64 hours at −40° C, the unstretched test-pieces give the same *x*-ray pattern as at room temperature in the case of natural rubber. With Neoprene-GN, an outer diffuse ring appears in the unstretched state.

In neither case is there any evidence of Debye rings, which would indicate random crystallization throughout the test-piece. If, therefore, random crystallites are present at all after 4–64 hours' storage at −40°C, they are too small to be detected by *x*-ray diffraction.

(2) After storage at −40° C, followed by stretching, diffraction spots appear with natural rubber at 200 elongation becoming rather more marked at

300. In addition, there is a slight increase in crystallinity on stretching from 4 hours to 64 hours' storage at the low temperature.

With Neoprene-GN, the diffraction spots on stretching after storage at −40° C are very well marked at 200 elongation, but no further increase in spot intensity is noticeable at 300 nominal elongation. There is similarly no apparent difference in orientation crystallization between the 4 and 64 hours' storage times.

With both rubbers, therefore, crystallization due to stretching occurs more readily at −40° C than at 21° C.

(C) Persistent After-effects at Room Temperature of Storage at −40° C

After storage at −40° C for 16 hours, followed by stretching to 200 elongation and warming up to room temperature, the test-pieces were exposed to *x*-rays, both in the stretched and then in the unstretched state at room temperature.

In the case of natural rubber there is no apparent difference between the above exposures made at 21° C and the corresponding exposures at 21° C made on rubber which had never been cooled to −40° C.

In the case of Neoprene-GN, the exposure at room temperature after storage at −40° C and then stretching to 200 per cent is similar to the corresponding photographs at 200 elongation on a test-piece which had never been cooled.

After storage and stretching at −40° C, followed by warming up to room temperature, the exposure of the unstretched test-piece shows an outer diffuse ring, where none was revealed in a test-piece which had never been cooled to −40° C.

SIMILARITIES BETWEEN NATURAL RUBBER AND NEOPRENE-GN

(1) Neither natural rubber nor Neoprene-GN in the unstretched state at −40° C show any evidence of the formation of random crystallites (Debye rings). This negative result may be due either to the insensitivity of the *x*-ray method in detecting small amounts of crystallization, particularly if only very small crystallites are formed; or it may be due to the nonformation of crystallites at −40° C, which is below the temperature for maximum rate of crystallization for both rubbers.

(2) Crystallization due to stretching occurs more readily at −40° C than at room temperature with both rubbers.

DIFFERENCE BETWEEN NATURAL RUBBER AND NEOPRENE-GN

(1) With natural rubber, the crystallization occurring on stretching at −40° C increases slightly with both degree of elongation and duration of storage at −40° C. With Neoprene-GN, the diffraction spots resulting on stretching at −40° C are not influenced by time of storage between 4 and 64 hours, and also appear to be independent of percentage elongation. In view of the fact that, at 21° C, the degree of crystallization of Neoprene-GN increases definitely with elongation, and also occurs more readily on stretching at −40° than at 21° C, the above result can only be attributed to the cracking and yielding of the frozen Neoprene-GN samples on first stretching.

Quite obviously there is no correspondence between 200 per cent elongation at 21° C and a nominal 200 per cent elongation after cracking and yielding.

It is a reasonable hypothesis that, at small nominal elongations (200–300 per cent) after yielding, the cold-drawn state of the test-piece will be about the same. This would adequately explain the apparently static nature of the diffraction pattern with degree of nominal elongation up to 300 per cent. The increased spot intensity with the frozen and stretched Neoprene-GN must be almost entirely due to the orientation produced by cold-drawing, since, at −40° C, the rubberlike elasticity is almost zero.

(2) Natural rubber unstretched at room temperature appears to have a more ordered structure than Neoprene-GN, but no persistent after-effects at room temperature appear to follow from the storage and stretching treatment at −40° C. With Neoprene-GN, on the other hand, storage and stretching (cold drawing) at −40° C produce a persistent after-effect at room temperature, as shown by the appearance of an outer diffuse ring.

CONCLUSIONS

The work reported on the low temperature shear deformation properties of natural rubber and Neoprene-GN gum compounds shows that, under the conditions of storage and applied stress investigated, there is little evidence of a yield effect with Neoprene-GN. It is suggested that the very large temperature-stiffening of this polymer is too great to give the yield effect under the low shear stresses studied. In tension, however, the yield effect is very marked with Neoprene-GN. On the other hand, a definite yield effect is shown as a result of shear deformation measurements on natural rubber stored at −40° C, whereas previous tension tests failed to detect this. It is shown that, under suitable conditions of storage time and at high shearing stresses, a natural rubber unit might fail in service by yielding and giving too much deflection. The more usual type of failure of a shear unit in service arises from loss of flexibility and hence deflection properties; the oil-resisting rubbers are particularly likely to suffer from this defect.

The *x*-ray data on natural rubber and Neoprene-GN gum compounds failed to reveal any evidence of random crystallite formation in the unstretched frozen rubbers. If the yield effect is due to crystallite formation in the unstretched state at low temperatures, then the crystallites are too small to be detected under the conditions of this investigation. In this connection, it is emphasized that a temperature of −40° C is below the temperature for maximum rate of development of crystallization for both rubbers.

With both natural rubber and Neoprene-GN, crystallization resulting from stretching occurs more readily and at lower elongations at −40° C than at room temperature. In the case of Neoprene-GN stored at −40° C and then stretched, crystallization does not increase with elongation as it does at room temperature. It is suggested that this is due to the cold-drawn state of Neoprene-GN on stretching after storage at −40° C.

These investigations have important practical and theoretical implications. Suggestions have often been made to include a test for crystallization in any characterization of compounds for low-temperature resistance. The results of the present work emphasize that the important factor is the time of storage at low temperature and the effects that this produces on crystallization and yield stress. The presence of crystallization is not so important as its continued development under long period exposure or its reorientation under applied stress.

ACKNOWLEDGMENT

The authors wish to express their thanks to A. F. Wells, for the help he gave with the x-ray work.

REFERENCES

[1] The Services Rubber Investigation, Users' Memorandum No. U.7.
[2] The Services Rubber Investigation, Users' Memorandum No. U.15.
[3] Bekkedahl and Wood, *J. Research Natl. Bur. Standards* **13**, 411 (1943).
[4] Liska, *Ind. Eng. Chem.* **36**, 40 (1944); RUBBER CHEM. & TECHNOL. **17**, 421 (1944); Forman, *Ind. Eng. Chem.* **36**, 738 (1944); The Services Rubber Investigation, Users' Memorandum No. U.15.
[5] Services Rubber Investigations, Users' Memoranda, with revisions and addenda, H. M. Stationery Office.

EFFECT OF TEMPERATURE ON RATE OF OXIDATION OF RUBBER
NATURE OF RESULTANT DETERIORATION *

J. Reid Shelton, Fred J. Wherley, and William L. Cox

Case Institute of Technology, Cleveland, Ohio

Accelerated tests are widely used to compare the relative resistance of rubber stocks to aging. These tests usually involve elevated temperature in the presence of air or oxygen, and may also involve increased pressure. It is frequently desired to translate the results of such short-term tests into predictions of probable aging behavior during storage or in service. Many observers have indicated, however, that a change of temperature frequently brings about a change in the nature of the aging[1]. For example, in the case of natural rubber, a change in the nature of the oxidation was suggested[2] in the vicinity of 70° to 80°C.

Kemp and coworkers[3] have demonstrated that, in the case of an uninhibited natural-rubber gum stock, the deterioration of tensile strength was a linear function of the amount of oxygen absorbed, as measured by the gain-in-weight method. The amount of oxygen required to produce a given deterioration varied linearly with the temperature, indicating a continuing change in the nature of the aging, rather than an abrupt change in the oxidation mechanism. The quantity of oxygen required to produce a given change in tensile decreased as the temperature of oxidation increased.

A direct relationship has also been observed in this laboratory[4] between the volume of oxygen absorbed, at constant temperature and pressure, and the changes of physical properties. A study of the effect of changes of temperature and of oxygen concentration on the rate of oxidation and the nature of the accompanying degradation was undertaken to see if the variations that result could be correlated in a regular fashion. If so, it should be possible to extrapolate the results obtained at higher temperatures in oxygen, so as to predict approximately the aging behavior in air at room temperature. The trends observed at different partial pressures of oxygen have been reported elsewhere[5], and this paper describes the effect of temperature variations with gum and black stocks of both natural rubber and GR-S.

EXPERIMENTAL PROCEDURE

The volumetric method of oxygen absorption was used. The equipment and procedure have been described in other papers from this laboratory[6].

Five stocks were studied—GR-S and Hevea, gum and black vulcanizates—as shown in Table I, including both inhibited and uninhibited stocks of the Hevea black. Samples were aged at four temperatures, 50°, 70°, 90°, and

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 9, pages 2080–2086, September 1953. The present address of F. J. Wherley is the B. F. Goodrich Research Center, Brecksville, Ohio.

TABLE I

COMPOSITION OF STOCKS

	Hevea stocks		GR-S stocks	
	Gum	Black[a]	Gum	Black
Smoked sheet	100	100	—	—
GR-S AC[b]	—	—	100	100
Paraflux[c]	—	4	—	4
Bardol[d]	—	—	—	4
Stearic acid	2	3	1	2.4
EPC black	—	50	—	45
Zinc oxide	5	3	5	2.4
Sulfur	3	3	2	2
Santocure[e]	—	1	1.2	1.2
Thiotax[e]	0.75	—	—	—
Santoflex B[e]	1.5	1.5	—	—
Cure time at 280°F (min.)	40	40	60	60

[a] Uninhibited Hevea black stock also included.
[b] Contains 1.25 per cent phenyl-2-naphthylamine.
[c] C. P. Hall Co.
[d] Barrett Division, Allied Chemical and Dye Co.
[e] Monsanto Chemical Co.

110°C, in oxygen at 1 atmosphere pressure. Dumbbell tensile-specimens, 4.5 inches long, were cut from sheets approximately 0.040 inch thick. Prior work[7] has shown that this thickness is satisfactory to avoid limitation by diffusion in the stage prior to the start of the autocatalytic stage. This study was confined to the earlier stages of oxidation, including the constant-rate stage, but not the final autocatalytic stage of rapid oxidation.

Triplicate samples were removed for testing after the absorption of a given amount of oxygen at the specified temperature. The maximum absorption in each case was usually less than 20 cc. of oxygen (25°C, 760 mm. of mercury) per gram of rubber hydrocarbon in the stock. This corresponds to about 2.6 per cent by weight, and while a rubber vulcanizate is capable of absorbing many times this amount of oxygen, the properties are degraded beyond practical use before this value is reached.

EFFECT OF TEMPERATURE ON RATE OF OXYGEN ABSORPTION

Examples of the oxidation curves obtained with the inhibited Hevea and GR-S black and gum stocks at 50° and at 110°C are shown in Figures 1 and 2. These curves are typical; first there is an initial rise, the size of which depends

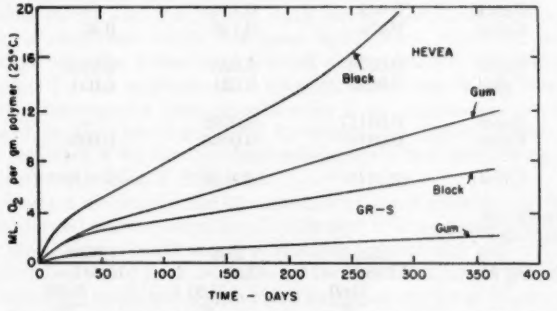


FIG. 1.—Oxygen absorption of Hevea and GR-S stocks at 50°C in oxygen at 760-mm. pressure.

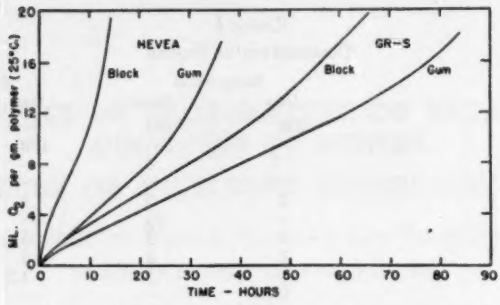


FIG. 2.—Oxygen absorption of Hevea and GR-S stocks at 110°C in oxygen at 760-mm. pressure.

on the recipe and previous history of the stock[8], followed by a slower constant-rate stage, and finally, if the test is continued long enough, the rate increases to a maximum in the autocatalytic stage. An equation has been fitted to the first two stages of the oxidation by Shelton and Winn[9], who give the equation for an absorption of V cc. of oxygen at constant temperature and pressures at time t:

$$V = V_0(1 - e^{-K_1 t}) + K_2 t$$

where K_2 is the rate of oxygen absorption in the constant-rate stage.

According to the Arrhenius equation, $K_2 = Ae^{-\Delta E^*/RT}$, and consequently, a plot of log K_2 *vs.* $1/T$ should give a straight line with an intercept equal to log A and a slope of $-\Delta E^*/2.303R$, if the type of rate-limiting reaction does not change with temperature. Such a plot for the Hevea black (inhibited and

TABLE II

RATE OF OXYGEN ABSORPTION IN CONSTANT-RATE STAGE AT VARIOUS TEMPERATURES

Temp. (°C)	Method of evaluation	K_2, cc. O_2 (25°C, 760 mm.) per g. polymer per hour: Hevea gum inhib.	Hevea black inhib.	Hevea black uninhib.	GR-S black inhib.
110	Exptl.	0.34	0.83	2.90	0.188
	Calcd.	0.32	0.79	2.85	0.19
100	Exptl.	—	0.36	1.18	0.089
	Calcd.	0.14	0.34	1.16	0.083
90	Exptl.	0.049	0.156	—	0.035
	Calcd.	0.059	0.145	0.45	0.034
70	Exptl.	0.0078	0.023	0.0545	0.0052
	Calcd.	0.0085	0.021	0.054	0.0052
50	Exptl.	0.00117	0.0022	—	0.00063
	Calcd.	0.0010	0.0026	0.0051	0.00057
25	Calcd.	4.8×10^{-5}	1.2×10^{-4}	1.7×10^{-4}	2.8×10^{-5}
Apparent energy of activation kcal./ mole		23.6	23.6	26.0	23.7
Equation for log K_2		$12.98-\frac{5160}{T}$	$13.37-\frac{5160}{T}$	$15.315-\frac{5690}{T}$	$12.78-\frac{5170}{T}$

uninhibited), Hevea gum, and GR-S black is shown in Figure 3. In every case a straight line fits the points over the temperature range studied (50° to 110°C). (Other studies in this laboratory have extended this relationship up to 150°C in the case of GR-S.) From this plot, apparent energies of activation, as well as equations for the rate of oxygen absorption of each as a function of the temperature, have been computed. These, together with a comparison of experimental and calculated rates, are presented in Table II. In the case of the Hevea black-inhibited stock, the results of five different batches, compounded to the same recipe, are included, and for GR-S black four different batches. Thus, the oxygen absorption data are fairly duplicable from batch to batch, though variation was noted in the 110°C results for the GR-S black stock, and the data for the GR-S gum stock were not sufficiently reproducible to be included here.

Figures 4 and 5 show plots of the logarithm of the time required to absorb certain volumes of oxygen as a function of the reciprocal of the absolute temperature, for Hevea black-inhibited and GR-S black stocks, respectively. (Such plots may be justified by consideration of the previously mentioned equation for an oxygen-absorption curve.) Included with each of these is a plot of the logarithm of the time required to reach the end of the constant-rate stage as a function of temperature. All such relationships are linear when plotted in this way. For both stocks, the volume of oxygen absorbed, before the end of the constant-rate stage is reached, increases as the temperature decreases. Many authors[10] attribute the end of this stage to the depletion of the antioxidant. It would seem reasonable that the total amount of oxygen actually reacting with antioxidant molecules should depend only on the amount of antioxidant present and not on the temperature. It is observed, however, that the amount of oxygen absorbed in the constant-rate stage by the whole stock (polymer and antioxidant) is greater at lower temperatures. Thus it would seem that a greater proportion of the oxygen is reacting with polymer at the lower temperature, while at the higher temperature a greater proportion of the oxygen is used up in reactions with the antioxidant.

This increased efficiency of the antioxidant at higher temperatures may also be seen by comparing the rates of oxygen absorption of inhibited and uninhibited Hevea black stocks at 110° and 70°C, as given in Table II. At 110°C, the uninhibited stock exhibits a rate 3.5 times greater than that of the inhibited stock, but at 70°C this factor is only 2.4. Similarly, comparing the calculated values at 25°C, it is seen that the rate of oxidation of the uninhibited stock would be only 1.4 times that of the inhibited stock.

The GR-S stocks and the Hevea black stocks contained Santocure as an accelerator, a substance which has some antioxidant character of its own. This, together with the presence of natural antioxidants in the Hevea stocks, would account for the existence of a constant-rate stage in an "uninhibited" stock, where theoretically none should exist if no antioxidant were present. This is based on the theory proposed by many investigators[11] that the antioxidant is responsible for the constant-rate stage which terminates when the antioxidant concentration is depleted.

This concept is also supported by unpublished work observed in this laboratory, which showed that a plot of log K_2 (the rate in the constant-rate stage) *vs.* $1/T°$ abs. for a Hevea black stock containing antioxidant and one not containing antioxidant could be represented by two lines in a manner comparable to the uninhibited and inhibited Hevea black stocks as shown in Figure 3. However, a similar plot of the reaction rates in the autocatalytic stage for the same

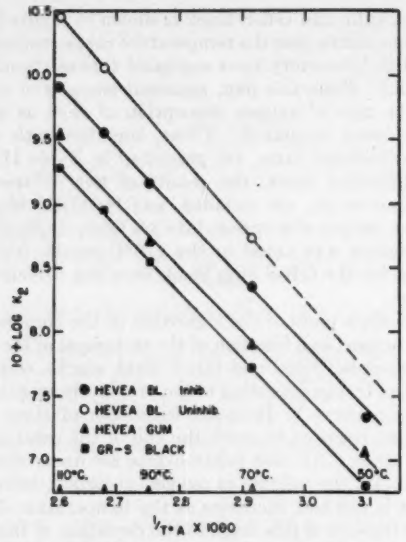


FIG. 3.—Effect of temperature on rate of oxygen absorption.
Log K_2 *vs.* $1/T°$ abs.

two Hevea stocks showed that a single line adequately represented the data for both. This would be expected if the antioxidant is depleted by the time the maximum rate in the autocatalytic stage is attained.

The linear relationships observed in the plots based on the Arrhenius equation (Figure 3), together with the linear plots (Figures 4 and 5) of the logarithm

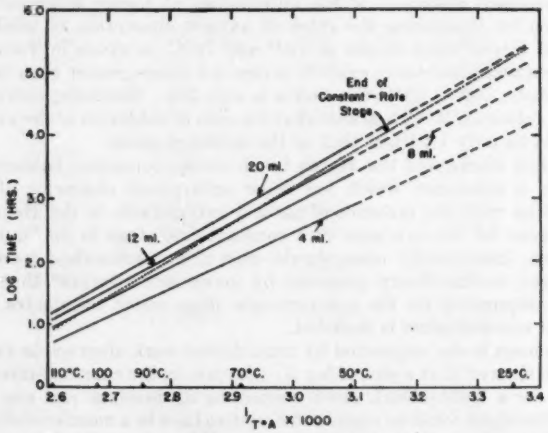


FIG. 4.—Time required to absorb given volume of oxygen at various temperatures.
Hevea black stock, log t *vs.* $1/T°$ abs.

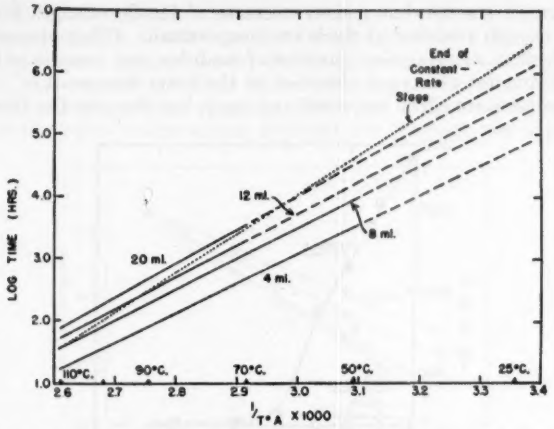


FIG. 5.—Time required to absorb given volume of oxygen at various temperatures. GR-S black stock, log t *vs.* $1/T^{\circ}$ abs.

of the time to absorb a given amount of oxygen as a function of the reciprocal of the absolute temperature, all tend to show that the rate-controlling reaction in the oxidation process is the same over the entire temperature range included in this study. The contrary conclusions found in the prior literature[12] can best be explained by considering also the effect of temperature on changes in physical properties accompanying oxidation, for these earlier studies were based on comparison of changes in properties after aging at different temperatures.

EFFECT OF TEMPERATURE ON DEGRADATION OF PROPERTIES ACCOMPANYING OXIDATION

GR-S Stocks.—The properties of a GR-S gum stock are generally so inferior, even before aging, that this type of stock is of little practical importance. In addition to this, the changes observed after oxidation were too erratic to be of significance, and consequently the data are not presented here.

The degradation of tensile strength of the GR-S black stock with oxygen absorption at various temperatures is shown in Figure 6. Some of the data are erratic, but in general the change is regular with oxygen absorption at a given temperature, and the effect of temperature is small in this case. The

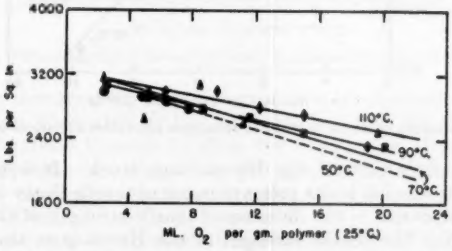


FIG. 6.—Tensile strength of GR-S black stock *vs.* oxygen absorption at various temperatures.

trend is toward a somewhat greater decrease of tensile strength for a given amount of oxygen absorbed at the lower temperature. Other properties show a greater decrease of elongation, increase of modulus, and increase of hardness, for a given amount of oxygen absorbed at the lower temperature. In every case the temperature effect was small and much less than for the Hevea black

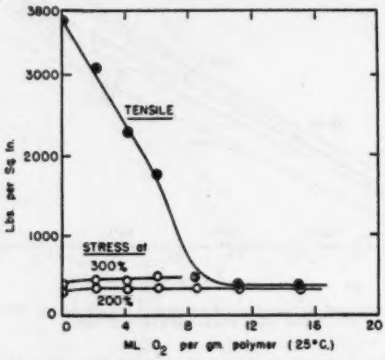


FIG. 7.—Change in physical properties of Hevea gum stock vs. oxygen absorption at 90°C.

stock. These changes reflect a stiffening of the GR-S black stock, which was observed at all temperatures studied, but the stiffening was slightly less for a given absorption of oxygen at the higher temperatures. This would be consistent with a higher proportion of chain scission at the higher temperatures. The temperature trend with tensile strength as shown for GR-S is reversed

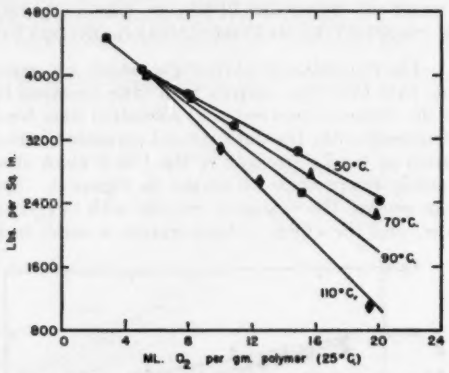


FIG. 8.—Tensile strength of Hevea black stock vs. oxygen absorption at various temperatures.

from the effect observed with the Hevea black stock. It would thus appear that, while chain scission is the primary cause of tensile decay in Hevea, cross-linking also contributes to the decrease of tensile strength of GR-S.

Hevea Stocks.—The tensile strength of the Hevea gum stock was rapidly degraded by a relatively small amount of oxygen. The behavior at 90°C, as

shown in Figure 7, is typical of the results obtained at all temperatures investigated. The absorption of only 1 per cent oxygen by weight (7.6 cc. of oxygen per gram of polymer) reduced the tensile strength from about 3700 pounds per square inch to a value of less than 1000, with the curve leveling off at about 400 pounds per square inch. A given amount of oxygen was about equally effective at the other temperatures, although the decrease was a little more

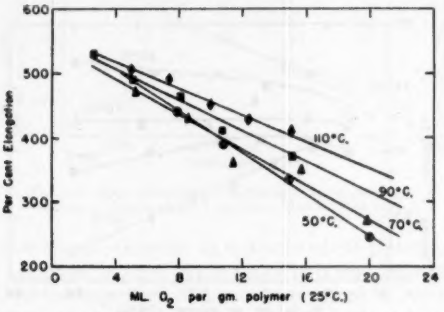


FIG. 9.—Ultimate elongation of Hevea black stock *vs.* oxygen absorption at various temperatures.

abrupt at the higher temperatures. Kemp and coworkers[13] observed a greater difference, but in the same direction, with an uninhibited gum stock. Chain scission is, of course, a major factor in tensile degradation, but other oxidation reactions which introduce irregularities in the chain, *e.g.*, cross-linking, would impede crystallization, and thus may account for much of the drastic reduction of tensile strength of the gum stock.

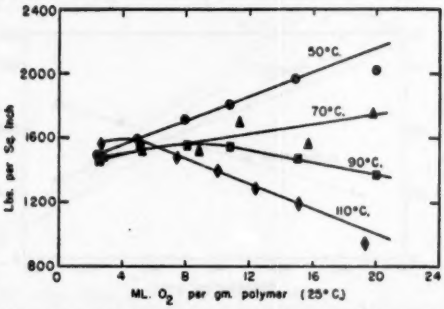


FIG. 10.—Modulus at 200% elongation of Hevea black stock *vs.* oxygen absorption at various temperatures.

The effect of temperature on the degradation of physical properties of a vulcanizate is best illustrated by the data obtained with the inhibited Hevea black stock. Figures 8 through 11 show the changes in physical properties (tensile strength, ultimate elongation, 200 per cent modulus, and Shore-A hardness) of this stock as a function of oxygen absorption for each of the four temperatures studied (50°, 70°, 90°, and 110° C). The slope of the linear portion of each curve thus represents the rate of change of this property with oxygen absorbed.

For a given oxygen absorption by this stock, tested at more than one temperature, a sample aged at a higher temperature shows lower tensile strength, lower modulus values, lower hardness, and higher elongation than an identical sample aged at a lower temperature. Thus, it would appear that chain scission predominates at higher temperatures, producing a softer stock having a lower modulus and greater elongation, whereas cross-linking predominates at lower

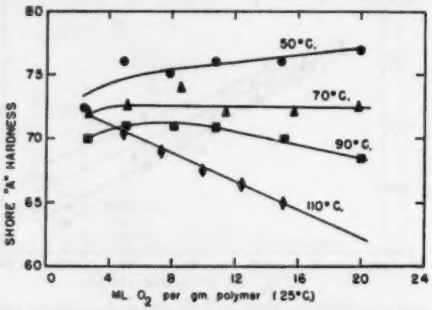


FIG. 11.—Shore-A hardness of Hevea black stock *vs.* oxygen absorption at various temperatures.

temperatures, giving a harder stock with a higher modulus and lower elongation. This would indicate the fallacy of predicting the aging characteristics of a stock at a low temperature from the result of accelerated aging at only one elevated temperature. It would also indicate that the steps which actually accomplish the degradation of a stock are not rate-controlling in the oxidation reaction, as no change is evident in the slope of the plots of log K_2 *vs.* $1/T$, a change which

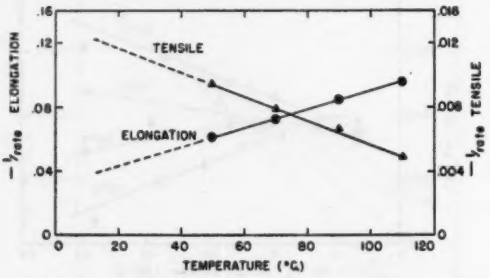


FIG. 12.—Rate of change of elongation and tensile values with temperature.
Per cc. of O_2 per gram of polymer, Hevea black stock.

is to be expected if the rate-controlling reaction changes. Thus degradation is a secondary reaction in the oxidative sense.

Figures 12 and 13 show the rates of change of the physical properties of the Hevea black inhibited stock with oxygen absorption as a function of the temperature at which they were aged. While the modulus rates are a linear function of the temperature, the reciprocals of the elongation and tensile rates must be employed in order to establish linearity with temperature. (An explanation of this relationship is presented below.) From an extrapolation of these rates,

it would appear that, at 25° C, after the initial variations due to cure, prior history, etc., have disappeared (about 4 to 5 cc. of oxygen absorbed per gram of polymer), the 200 and 300 per cent moduli would continue to increase with further oxygen absorption at the rate of 70 and 85 pounds per square inch per cc. of oxygen per gram of polymer, respectively, while the tensile strength and

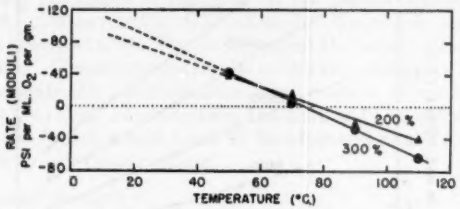


FIG. 13.—Rate of change of modulus with temperature.
Per cc. of O_2 per gram of polymer, Hevea black stock.

ultimate elongation would decrease at the rate of 89 pounds per square inch and 22 per cent per cc. of oxygen per gram of polymer, respectively.

Figure 14 shows the logarithm of the time required to reach a given tensile strength as a function of the reciprocal of the absolute temperature. This would give an extrapolated value of approximately 20 years at 25° C to degrade

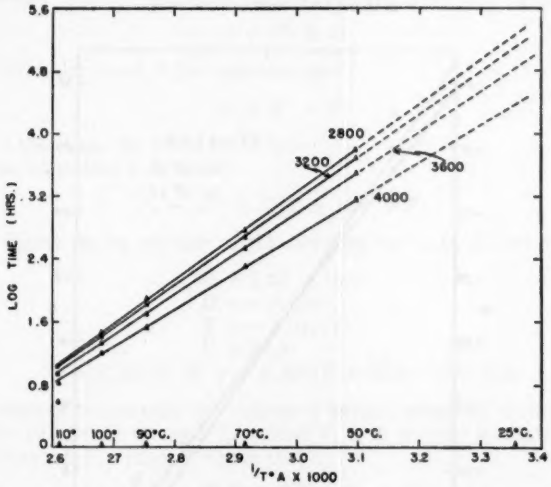


FIG. 14.—Time required to reduce tensile strength to a given value at various temperatures.
Hevea black stock, log t *vs.* $1/T°$ abs.

the tensile strength of Hevea black stock of this compounding to a value of 2800 pounds per square inch.

Figure 15 shows the volume of oxygen necessary to reduce the tensile strength of this Hevea black stock to a given value as a function of the centigrade temperature. For each given value of the tensile strength, the result is a

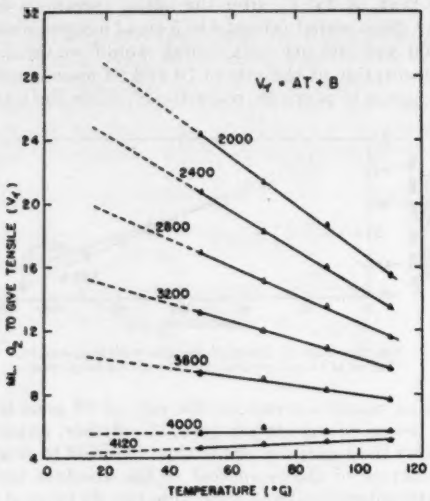


FIG. 15.—Volume of oxygen required at various temperatures to reduce tensile of Hevea black stock to given value.

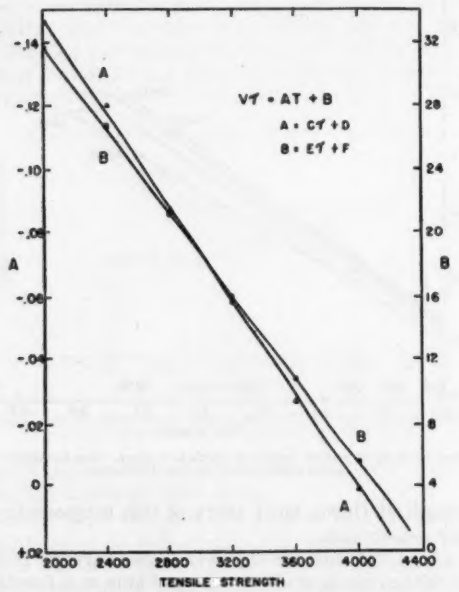


FIG. 16.—Slopes and intercepts from Figure 15 as function of tensile strength.

straight line which may be extrapolated. Thus it appears that approximately 19 cc. of oxygen per gram of polymer must be absorbed at 25° C to degrade the tensile strength to 2800 pounds per square inch. From Figure 4, this would be in the neighborhood of 18 to 19 years, a value checking that given by Figure 14, as stated above. By inspection of Figure 15, it is seen that both the slopes of the lines and the intercepts of the lines on the volume axis change with the tensile selected. Consequently, the values for the slopes and intercepts of Figure 15 have been plotted in Figure 16 against the tensile strength. The plot is linear for both. Therefore, the results of the two plots may be combined, as follows, to interrelate the three variables (temperature, oxygen absorption, and tensile strength), so that, knowing two, the third may be calculated—*e.g.*, the volume of oxygen which would need to be absorbed at 25°C to degrade the tensile strength to any desired value.

Let τ = tensile strength
V_τ = oxygen absorption giving tensile strength τ
T = temperature of reaction, ° C

In Figure 15, the expression for the volume of oxygen, V, required to reduce the tensile strength to a value τ at temperature T is:

$$V_\tau = AT + B \tag{1}$$

i.e., the expression for a straight line with slope A and intercept B. But we have seen that A and B are linear functions of τ (Figure 16). Thus:

$$A = C\tau + D \tag{2}$$

where C is the slope and D the intercept, and:

$$B = E\tau + F \tag{3}$$

where E is the slope and F the intercept.
Thus, from Equations 1, 2, and 3:

$$V_\tau = (C\tau + D)T + (E\tau + F) \tag{4}$$

From Figure 16, we are able to obtain values for C, D, E, and F:

$$C = 7.35 \times 10^{-5}$$
$$D = -\ 0.294$$
$$E = -\ 0.01315$$
$$F = 58.0$$
$$V_\tau = (7.35 \times 10^{-5}\tau - 0.294)T + 58.0 - 0.01315\tau$$

which enables us to compute the volume of oxygen necessary at any temperature to give any tensile strength (provided $V_\tau > 4$, in order to eliminate initial effects of cure, etc.). From 4 we see that:

$$V_\tau = C\tau T + DT + E\tau + F$$
$$V_\tau = (CT + E)\tau + (DT + F) \tag{5}$$

At constant temperature:

$$V_\tau = \alpha\tau + \beta$$

where:

$$\alpha = CT + E$$
$$\beta = DT + F$$

The rate of tensile decay with oxygen absorption at one temperature, k_τ, is given by the difference in tensile strength at two absorptions divided by the difference in absorption, or

$$k_\tau = \frac{\tau_1 - \tau_2}{V_{\tau_1} - V_{\tau_2}} = \frac{\tau_1 - \tau_2}{\alpha\tau_1 + \beta - \alpha\tau_2 - B} = \frac{\tau_1 - \tau_2}{\alpha(\tau_1 - \tau_2)} = \frac{1}{\alpha} = \frac{1}{CT + E}$$

Thus the reciprocal of the rate should be a linear function of the temperature, as was shown to be the case in Figure 12. Moreover, k_τ's calculated from values of C, T, and E closely correspond with experimental values.

It is, therefore, possible to extrapolate oxygen-absorption and aging data obtained at several temperatures to predict the behavior under comparable conditions at other temperatures. The work described here has been confined to aging in an atmosphere of pure oxygen. A change to a mixture of oxygen and nitrogen as found in air will, of course, also affect the rate of oxidation. This effect of oxygen concentration has been presented in a separate communication[5]. Taking into account changes in both temperature and pressure, it is possible to interpret the results of accelerated tests in oxygen in terms of the behavior to be expected in air at normal storage temperatures. The quantitative relationships would have to be established for each stock, but the qualitative trends are apparent from the results described in this paper and related studies referred to above.

SUMMARY AND CONCLUSIONS

The same reaction appears to be rate-controlling in the oxidation of natural rubber and GR-S stocks at all temperatures in the range studied, 50° to 110° C. This is apparent from the linear relationship established between rate of oxygen absorption and the reciprocal of the absolute temperature. Presumably this would also be true for a reasonable extrapolation to lower or higher temperatures. Thus it is possible to determine the probable rate of oxygen absorption at room temperature on the basis of data obtained in short-term tests at higher temperatures, provided data are available at several temperatures.

The effect on properties which accompanies the absorption of a given amount of oxygen varies with the temperature. For example, aging at higher temperatures produces a softer stock with lower modulus and higher elongation than is obtained by the absorption of the same amount of oxygen at a lower temperature. Thus chain scission predominates at higher temperatures, while crosslinking becomes of greater relative importance at lower temperatures. These facts, together with the observation that the same reaction is rate-controlling at all temperatures studied, indicate that the degradation reactions must be secondary reactions which are not rate-controlling.

One cannot predict the aging characteristics of a stock by the use of an accelerated test at only one temperature. It is possible, however, to establish a quantitative measure of the rate of change in a given property (per unit amount of oxygen absorbed) as a function of temperature by means of tests at more than one temperature. Thus it is now possible to utilize short-term oxygen-absorption measurements at, say, three temperatures to establish the relationships, and then to extrapolate the data to lower temperatures and predict the time required to absorb a given amount of oxygen and the degradation of properties to be expected under comparable conditions at the lower temperature. If a change from oxygen to air is also involved, the effect of the changes in oxygen concentration must also be taken into account.

ACKNOWLEDGMENT

The work reported here was obtained as a part of a research project on oxidation and aging of natural and synthetic rubber sponsored by Army Ordnance. The work was done in the laboratories of the Department of Chemistry and Chemical Engineering at Case Institute of Technology in collaboration with the Firestone Tire and Rubber Co.

REFERENCES

[1] Davy, *Trans. Inst. Rubber Ind.* **5**, 386 (1930); RUBBER CHEM. & TECHNOL. **3**, 563 (1930); Williams and Neal, *Ind. Eng. Chem.* **22**, 874 (1930); RUBBER CHEM. & TECHNOL. **3**, 678 (1930); Yamazaki and Okayama, *J. Soc. Chem. Ind. Japan* **33**, 68 (1930); RUBBER CHEM. & TECHNOL. **3**, 378 (1930); Milligan and Shaw, *Proc. Rubber Tech. Conf. London*, **1938**, p. 537; RUBBER CHEM. & TECHNOL. **12**, 235 (1939); Morgan and Naunton, *Proc. Rubber Tech. Conf. London*, **1938**, p. 599; RUBBER CHEM. & TECHNOL. **12**, 235 (1939); Kemp, Ingmanson, and Mueller, *Ind. Eng. Chem.* **31**, 1372 (1939); RUBBER CHEM. & TECHNOL. **13**, 375 (1940); Shelton and Winn, *Ind. Eng. Chem.* **39**, 1133 (1947); RUBBER CHEM. & TECHNOL. **21**, 180 (1948); Scott, *J. Rubber Research* **18**, 117 (1949); RUBBER CHEM. & TECHNOL. **23**, 390 (1950).

[2] Davy, *Trans. Inst. Rubber Ind.* **5**, 386 (1930); RUBBER CHEM. & TECHNOL. **3**, 563 (1930); Yamazaki and Okayama, *J. Soc. Chem. Ind. Japan* **33**, 68 (1930); RUBBER CHEM. & TECHNOL. **3**, 378 (1930); Morgan and Naunton, *Proc. Rubber Tech. Conf. London*, **1938**, p. 599; RUBBER CHEM. & TECHNOL. **12**, 235 (1939).

[3] Ingmanson and Kemp, *Ind. Eng. Chem.* **30**, 1168 (1938); Kemp, Ingmanson, and Mueller, *Ind. Eng. Chem.* **31**, 1472 (1939); RUBBER CHEM. & TECHNOL. **13**, 375 (1940).

[4] Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946); RUBBER CHEM. & TECHNOL. **19**, 696 (1946); Shelton and Cox, *Ind. Eng. Chem.* **43**, 456 (1951); RUBBER CHEM. & TECHNOL. **24**, 981 (1951).

[5] Shelton and Cox, *Ind. Eng. Chem.* **45**, 392; RUBBER CHEM. & TECHNOL. **24**, 981 (1951).

[6] Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946); RUBBER CHEM. & TECHNOL. **19**, 696 (1946); Winn, Shelton ,and Turnbull, *Ind. Eng. Chem.* **38**, 1050 (1946); RUBBER CHEM. & TECHNOL. **20**, 469 (1947); Blum, Shelton, and Winn, *Ind. Eng. Chem.* **43**, 464 (1951); RUBBER CHEM. & TECHNOL. **24**, 999 (1951).

[7] Blum, Shelton, and Winn, *Ind. Eng. Chem.* **43**, 464 (1951); RUBBER CHEM. & TECHNOL. **24**, 999 (1951).

[8] Stafford, *Proc. 2nd Rubber Tech. Conf. London*, **1948**, p. 94; RUBBER CHEM. & TECHNOL. **23**, 404 (1950).

[9] Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946); RUBBER CHEM. & TECHNOL. **19**, 646 (1946).

[10] Carpenter, *Ind. Eng. Chem.* **39**, 187 (1947); RUBBER CHEM. & TECHNOL. **20**, 728 (1947); Kuzminskiĭ and Leshnev, *Doklady Akad. Nauk USSR* **69**, 557 (1949); *Zhur. Fiz. Khim.* **24**, 539 (1950); Blum, Shelton, and Winn, *Ind. Eng. Chem.* **43**, 464 (1951); RUBBER CHEM. & TECHNOL. **24**, 999 (1951).

[11] Carpenter, *Ind. Eng. Chem.* **39**, 187 (1947); RUBBER CHEM. & TECHNOL. **20**, 728 (1947); Blum, Shelton, and Winn, *Ind. Eng. Chem.* **43**, 464 (1951); RUBBER CHEM. & TECHNOL. **24**, 999 (1951).

[12] Davey, *Trans. Inst. Rubber Ind.* **5**, 386 (1930); RUBBER CHEM. & TECHNOL. **3**, 563 (1930); Williams and Neal, *Ind. Eng. Chem.* **22**, 874 (1930); Yamazaki and Okayama, *J. Soc. Chem. Ind. Japan* **33**, 68 (1930); RUBBER CHEM. & TECHNOL. **3**, 378 (1930); Morgan and Naunton, *Proc. Rubber Tech. Conf. London*, **1938**, p. 599; RUBBER CHEM. & TECHNOL. **12**, 245 (1939).

[13] Kemp, Ingmanson, and Mueller, *Ind. Eng. Chem.* **31**, 1472 (1939); RUBBER CHEM. & TECHNOL. **13**, 375 (1940).

MERCAPTOBENZOTHIAZOLE VULCANIZATION USING SULFUR[35] *

IRVING AUERBACH

THE GOODYEAR TIRE AND RUBBER CO., AKRON, OHIO

Since the discovery of the accelerating properties of mercaptobenzothiazole (MBT), a number of mechanisms have been suggested to account for its role[1]. The formulation of these mechanisms was hampered from the very beginning, because the process of vulcanization itself was not well understood. Furthermore, intermediates were suggested whose presence was not assured. In the light of newer information on the mechanism of vulcanization and because of the possibilities opened up by tracer techniques, a re-examination of this problem was undertaken.

EXPERIMENTAL WORK

By using either radioactive elementary sulfur or mercaptobenzothiazole in which the mercapto group was tagged, the analytical procedures were greatly simplified and very rapidly performed. Thus, it was possible to extract vulcanized samples containing tagged mercaptobenzothiazole with alcohol, determine consumed mercaptobenzothiazole, and then extract again the same samples with chloroform to determine mercaptobenzothiazole combined as the zinc mercaptide. Similarly, combined sulfur was determined by using radioactive sulfur in the vulcanization formula. Extracting with acetone and determining the residual activity in the vulcanizate gave the total combined sulfur. By extracting again with an alcohol-ether solution of hydrochloric acid, zinc sulfide was removed. The residual activities of the samples then indicated organically combined sulfur. The term *consumed mercaptobenzothiazole* refers to mercaptobenzothiazole products not soluble in alcohol and combined sulfur includes rubber-sulfur compounds and zinc sulfide.

The test-specimens were prepared in the following manner. GR-S, containing 4.78 per cent fatty acid, or unextracted pale crepe, was dissolved in benzene with the aid of heat and stirring. Zinc oxide which had been dispersed by milling into raw stock (50–50) was then suspended in this solution. Sulfur and mercaptobenzothiazole dissolved in benzene were added to the cool suspension. After stirring for about 30 minutes, the cement was poured on aluminum foil, the benzene was allowed to evaporate, and the compounded rubber was stripped from the foil. Stripping was facilitated by coating the foil with a very thin soap film before pouring the cement.

The amount of consumed mercaptobenzothiazole or, more strictly, the consumed sulfur from the mercaptobenzothiazole mercaptan group, was measured by curing duplicate samples containing radioactive mercaptobenzo-

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 7, pages 1526–1532, July 1953. The work is part of a research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the synthetic rubber program. The paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Buffalo, N. Y., October 29–31, 1952.

thiazole in mold cavities 1.5 inches in diameter at ca. 20,000 pounds per square inch for various time intervals; 30 to 45 seconds was allowed for the sample to come to press temperature. Then 1¾-inch disks were stamped out. These were approximately 0.025 inch thick and corresponded to infinite thickness for sulfur radioactivity measurements. Radioactivity measurements were made on both sides in a windowless proportional flow counter and the four values averaged. The samples were then extracted with absolute alcohol for 24 hours. The radioactivity of the rubber was redetermined and the per cent consumed mercaptobenzothiazole calculated from these values.

Combined sulfur was determined by making additional cures under identical conditions with a recipe containing radioactive free sulfur. These were extracted with acetone. The per cent combined sulfur was determined from activities before and after extraction. All cures were performed at 140° C unless otherwise stated.

This experimental procedure possesses several advantages. It is simple, rapid, and nondestructive, thereby allowing several different analyses with the same sample. Furthermore, it allows for the determination of combined sulfur which originated from the free sulfur independent of that from the accelerator sulfur.

FREE SULFUR-ACCELERATOR SULFUR INTERCHANGE

The analytical results are of significance only if there is no appreciable exchange between mercaptobenzothiazole sulfur and free sulfur. This was shown in several experiments. Hevea stock containing zinc oxide, sulfur, and mercaptobenzothiazole in the same amounts used for the work was cured for various time intervals up to 120 minutes. Combined sulfur was complete after about 60 minutes. The mercaptobenzothiazole was extracted and the specific activity determined. The average specific activity of the extracted mercaptobenzothiazole was $1.45 \pm 0.08 \times 10^4$ counts per minute per mg. The activity of the original mercaptobenzothiazole was 1.43×10^4 counter per minute per mg. No trend in specific activity with curing time was noted, indicating that the recovered mercaptobenzothiazole had not undergone exchange.

INITIAL VULCANIZATION REACTIONS

The effect of variations in the mercaptobenzothiazole, sulfur, and zinc oxide concentrations on the sulfur combining rate was determined. A base formula of 100 parts of GR-S, 3 parts of zinc oxide, 3 parts of sulfur, and 1 part of mercaptobenzothiazole was adopted. The sulfur, mercaptobenzothiazole, and zinc oxide concentrations were then varied individually. Figures 1 to 4 give curves which are representative of the results obtained. They show the variation of consumed mercaptobenzothiazole and combined sulfur with time and, in two cases, the variation of the zinc mercaptide of mercaptobenzothiazole with time. In these figures, the reacted quantities of vulcanization ingredients are given as the per cent of the formula weight.

With the exception of Figure 4, the results show a marked induction period for the sulfur reaction. The consumed mercaptobenzothiazole is regenerated rapidly and goes through a minimum, after which it is once more consumed by the rubber in a manner paralleling the sulfur reaction.

Several relationships are apparent. Thus the times at which the minimum occurs and the sulfur reaction starts are approximately the same. Second, in Figure 3 where 5 parts of sulfur per 100 parts of rubber is present, the minimum

occurs at approximately 8 minutes, whereas in Figure 2 where 1 part of sulfur is present the minimum occurs at 60 minutes. Third, Figures 1 and 3, where 3 and 5 parts of zinc oxide per 100 parts of rubber were used, show that the quantity of consumed mercaptobenzothiazole at zero time is greatly enhanced by the presence of the larger quantity of zinc oxide. In Figure 4 where 5 parts of mercaptobenzothiazole is present the reaction is very rapid, the sulfur having

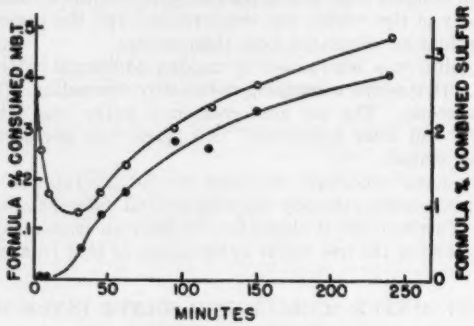


FIG. 1.—Consumed mercaptobenzothiazole and combined sulfur. Formulation. GR-S 100, zinc oxide 5, sulfur 3, MBT 1

○ Consumed MBT
● Combined sulfur

reacted completely after 45 minutes. It is believed that the induction period for the sulfur reaction and the minimum for the mercaptobenzothiazole reaction are absent for this reason.

In the tests illustrated in Figures 3 and 4, the vulcanized samples were extracted again with chloroform to remove any zinc mercaptide of mercaptobenzothiazole. Figure 3 shows that no mercaptobenzothiazole zinc mercaptide is present beyond the minimum until after 150 minutes' curing time. However,

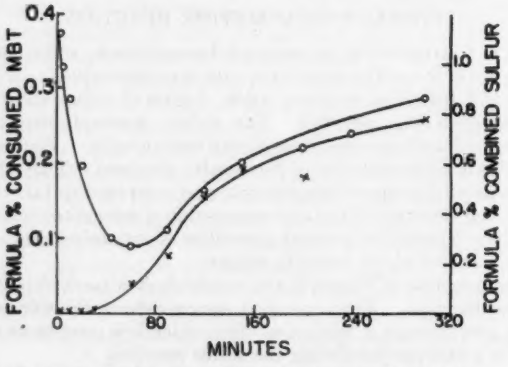


FIG. 2.—Consumed mercaptobenzothiazole and combined sulfur. Formulation. GR-S 100, zinc oxide 3, sulfur 1, MBT 1

○ Consumed MBT
× Combined sulfur

when 5 parts of mercaptobenzothiazole per 100 parts of rubber was used, Figure 4, a large quantity of the mercaptide was present.

This information suggests that the primary mercaptobenzothiazole product is the zinc mercaptide, since an increase in zinc oxide from 3 to 5 parts would be expected to give 3.34-fold increase of alcohol-insoluble mercaptobenzothiazole. The observed increase was 3.38-fold. The figures also suggest that a reaction

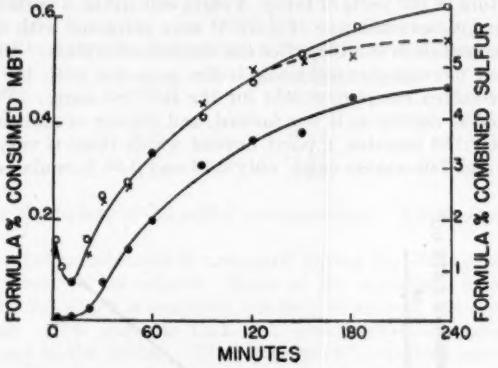


FIG. 3.—Consumed mercaptobenzothiazole and combined sulfur. Formulation. GR-S 100, zinc oxide 3, sulfur 5, MBT 1

● Combined sulfur
○ MBT not extracted by alcohol
× MBT not extracted by chloroform

takes place between the mercaptobenzothiazole zinc mercaptide and sulfur, as increasing the sulfur concentration correspondingly decreases the time at which the minimum is reached. Thus for the experiments involving 1, 3, and 5 parts of sulfur, the minima were obtained at approximately 60, 18, and 8 minutes. No minimum was obtained, however, for the case where 0.5 part of sulfur per 100 parts of rubber was used. This initial reaction may be accounted for by

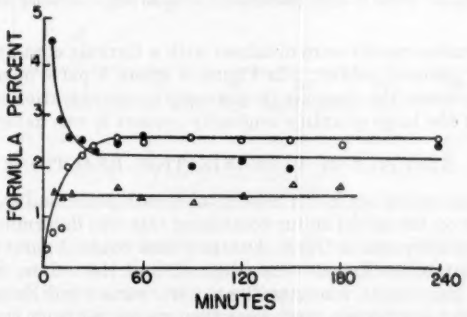


FIG. 4.—Consumed mercaptobenzothiazole and combined sulfur. Formulation. GR-S 100, zinc oxide 3, sulfur 3, MBT 5

○ Combined sulfur
● MBT not extracted by alcohol
△ MBT not extracted by chloroform

the formation of hydrogen sulfide in sufficient quantities to inhibit the sulfur-rubber reaction. It would be removed by reaction with the mercaptide to regenerate mercaptobenzothiazole[2].

As the mercaptobenzothiazole zinc mercaptide reacts so readily, it might be anticipated that its concentration would be very small, even though mercaptobenzothiazole is regenerated and probably reacts with more zinc oxide or zinc stearate. This was confirmed when the vulcanized samples from the compounded mixture of 100 parts of GR-S, 3 parts zinc oxide, 5 parts of sulfur, and 1 part of mercaptobenzothiazole (Figure 3) were extracted with chloroform, in which the mercaptide is soluble, after the alcohol extraction. Figure 3 shows that consumed mercaptobenzothiazole is the same for both the alcohol- and chloroform-extracted samples, except for the last few cures. Thus the mercaptide reacted as rapidly as it was formed, and did not accumulate to any extent until after 150 minutes, a point beyond which there is very little sulfur. For the 180- and 240-minute cures, only 0.18 and 0.04 formula-per cent sulfur

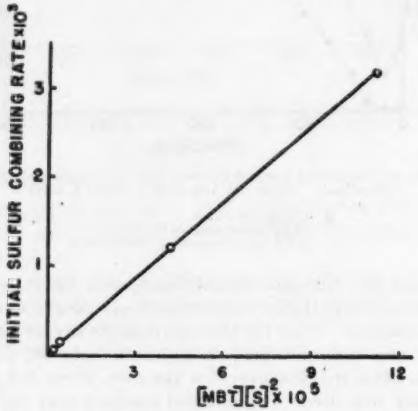


FIG. 5.—Effect of sulfur concentration on initial sulfur-combining rate.

remained. Similar results were obtained with a formula containing 0.5 part of sulfur per 100 parts of rubber. In Figure 4 where 5 parts of mercaptobenzothiazole was present, the decrease in mercaptide concentration was very rapid, and because of the large quantity originally present it was never depleted.

KINETICS OF VULCANIZATION REACTIONS

The effect of variations in the mercaptobenzothiazole, sulfur, and zinc oxide concentrations on the initial sulfur combining rate was determined. The same base formula of 100 parts of GR-S, 3 parts of zinc oxide, 3 parts of sulfur, and 1 part of mercaptobenzothiazole was adopted, and the sulfur, mercaptobenzothiazole, and zinc oxide concentrations were varied individually as before. The initial sulfur combining rates were then measured from the plots of combined sulfur *vs.* time. These values are given in Table I, as moles of combined sulfur per 100 grams of vulcanizate per minute. The concentrations of the various reactants are listed, for convenience, as parts per 100 grams of GR-S.

Variation of the zinc oxide concentration does not affect the rate at which sulfur reacts over this range. This would seem to indicate that this reactant is not involved in the rate-determining step at these concentrations. The effect of the mercaptobenzothiazole on the sulfur combining rate is linear. A five-fold increase of the mercaptobenzothiazole concentration increased the rate approximately five times. A linear relationship was also noted in data obtained by Adams[3] with natural rubber. With respect to sulfur, however, the rate is

TABLE I

EFFECT OF REACTANT CONCENTRATION ON INITIAL SULFUR COMBINING RATE

Percentage	(Combining rate $\times 10^{-3}$ mole/100 grams/minute) MBT	Zinc oxide	Sulfur
0.5	—	—	0.052
1	1.19	1.12	0.156
3	—	1.19	1.19
5	6.79	1.05	3.20

proportional to the square of the sulfur concentration. This is shown graphically in Figure 5.

That mercaptobenzothiazole is consumed during the vulcanization process has also been observed by others[4]. Some of the consumed mercaptobenzothiazole is in a form which is insoluble, not only in alcohol, but also in acetone and chloroform. This suggests that this mercaptobenzothiazole might be chemically bound to the rubber. That the ratio of consumed mercaptobenzo-

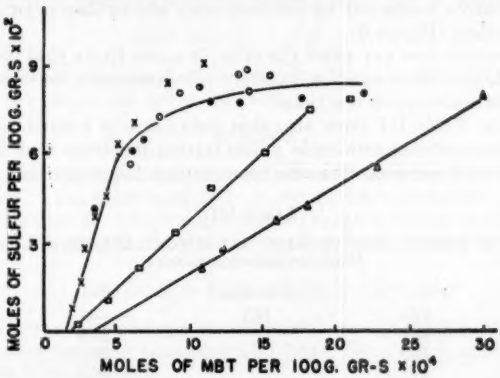


FIG. 6.—Variation of combined sulfur with consumed mercaptobenzothiazole

Hevea. X, 120°C; ●, 140°C; ○, 160°C
GR-S. □ 140°C, rapid curing stock
△ 140°C slower curing stock
Composition. Sulfur 3, zinc oxide 3, MBT 1 per 100 parts of rubber

thiazole to combined sulfur is constant was made evident when the consumed mercaptobenzothiazole was plotted against combined sulfur. Straight lines were obtained in all cases except where curing proceeded rapidly, and most of the data obtained consisted of values after curing was almost complete.

If the consumed mercaptobenzothiazole and combined sulfur are divided by their respective molecular and atomic weights and these values are plotted, the slopes of the straight lines obtained indicate the number of atoms of sulfur

which combine with the rubber or zinc per molecule of mercaptobenzothiazole consumed. Typical plots are shown in Figure 6 and the slopes are given in Table II. Where curing had proceeded rapidly, the ratios were obtained by averaging the ratios for the individual cures.

The ratio of combined sulfur to consumed mercaptobenzothiazole is independent of the temperature. This is brought out clearly in the case of GR-S, (Table III). Data were obtained at three temperatures with the following formulation: 3 parts of sulfur, 3 parts of zinc oxide, and 1 part of mercaptobenzothiazole per 100 parts of rubber. Curing proceeded slowly enough so that sufficient data could be obtained with pale crepe at 120° C. At higher tem-

TABLE II

RATIO OF COMBINED SULFUR TO CONSUMED MERCAPTOBENZOTHIAZOLE–GR-S

Percentage	MBT	ZnO	S
0.5	—	—	15.0
1	43.3	13.2	17.1
3	—	43.3	43.3
5	6.5	34.0	52.8
	4.1[a]		

[a] Values obtained with slower curing GR-S Stock.

peratures, however, the curing was practically complete within the first few minutes. The data could not be averaged as in the case of GR-S, since mercaptobenzothiazole continued to combine with the rubber even after all the sulfur had reacted (Figure 6).

As temperature does not affect the ratio, it seems likely that both reactants are involved in the same reaction, possibly simultaneously, but more probably in some sort of consecutive reactions.

The data in Table III show also that pale crepe is a much more efficient medium for mercaptobenzothiazole vulcanization reactions than is GR-S. A slower rate of mercaptobenzothiazole consumption might account for the large

TABLE III

EFFECT OF TEMPERATURE ON RATIO OF COMBINED SULFUR TO CONSUMED MERCAPTOBENZOTHIAZOLE

Temp. (°C)	Pale crepe	GR-S
120	165	—
130		26.8
140		26.9
150		28.6

difference in the ratio of sulfur to mercaptobenzothiazole for pale crepe and GR-S. It was found, however, that mercaptobenzothiazole is consumed more rapidly with pale crepe.

Deviations from straight lines were noted in several cases where one of the reactants had been depleted. When the pale crepe medium was used, all of the sulfur reacted; mercaptobenzothiazole, however, continued to be consumed (Figure 6). In the series of cures with GR-S (Table II) using 1 part of zinc oxide per 100 parts of rubber, all of the mercaptobenzothiazole was consumed, yet sulfur continued to react with the rubber. In Figure 4, however, the sulfur and mercaptobenzothiazole reactions appear to have terminated at the same time.

Of further interest is the observation that mercaptobenzothiazole is consumed before the sulfur reaction begins. This is indicated by the intercept of the lines in Figure 6. The intercept values are given in Table IV for the experiments conducted with GR-S.

For the pale crepe stock, the intercept occurred at 1.4×10^{-4} mole of mercaptobenzothiazole. These results indicate that some of the mercaptobenzothiazole forms an alcohol-insoluble compound in the initial stages of vulcanization before any sulfur has had a chance to react. The data correspond to the values of the consumed mercaptobenzothiazole at the minima in Figures 1 to 3.

From the data given in Table I, a kinetic expression can be given for the sulfur combining rate, which at least empirically accounts for the initial vul-

TABLE IV

MERCAPTOBENZOTHIAZOLE CONSUMED PRIOR TO THE SULFUR REACTION

Percentage	MBT	ZnO	S
0.5	—	—	3.3
1	1.7	4.0	2.8
	2.0[a]		
3	—	1.7	1.7
5	—	2.6	8.5

[a] Slower curing GR-S stock.

canization reaction. If a and b represent the initial mercaptobenzothiazole and sulfur concentrations and y and x reacted with mercaptobenzothiazole and sulfur, respectively, then the equation relating them can be written as:

$$dx/dt = k_1(a - y)(b - x)^2 \tag{1}$$

As the ratio of consumed mercaptobenzothiazole to combined sulfur is constant, as is represented in the following:

$$x/y = r \tag{2}$$

Equation 1 can be changed into an equation with a single dependent variable and integrated. The integrated form of this equation, however, did not satisfactorily account for the data for an extended range of vulcanization beyond the initial stage. An equation which does reproduce the experimental results in this range is:

$$dx/dt = k_2b(a - y)(b - x)^{\frac{1}{2}} \tag{3}$$

Equation 3 was tested by graphical integration using experimental values of x and y and also by using the integrated form, Equation 4, after substituting x/r for y from Equation 2.

$$\frac{2r}{(ar - b)^{\frac{1}{2}}}\left[\tan^{-1}\frac{-(b - x)^{\frac{1}{2}}}{(ar - b)^{\frac{1}{2}}} - \tan^{-1}\frac{-b^{\frac{1}{2}}}{(ar - b)^{\frac{1}{2}}}\right] = bk_2t \tag{4}$$

The values of k_2 obtained by graphical integration are given in the fourth column of Table V. Values calculated from Equation 4 are given in columns two and three.

Although the average deviations for the rate constants varied between 10 and 20 per cent, they are not indicative of any trend in the rate constant with time. This is shown in Table VI, where the individual constants for the series of cures involving 5 parts of sulfur per 100 parts of rubber are given. This experiment was chosen because it covers the largest range of reacted sulfur,

TABLE V

EFFECT OF REACTANT CONCENTRATION ON RATE CONSTANT, k_2

Percentage	(100 gram-mole$^{-1/2}$ minute^{-1}) MBT	Zinc Oxide	Sulfur
0.5	—	—	5.32
1.0	5.78	5.58	5.03
3.0	6.93	5.78	5.98
5.0	6.93	6.29	7.25
	3.46[a]		

[a] Experiments conducted with a slower curing stock, emphasizing the independence of the rate constant on MBT concentration.

4.8 to 99.1 per cent. The curing times given have been corrected for the induction period.

The sulfur combining reaction follows Equation 1 initially and Equation 3 for the remainder of the reaction. This indicated that sulfur is being used up faster than would be predicted by Equation 1 and suggests that the reaction product of the sulfur-rubber reactions is also reacting with sulfur.

The rate of this secondary reaction is the difference in the rates obtained from Equations 1 and 3 for any given value of x. It is, therefore, possible to determine these rates, since k_1 can be obtained from Figure 5 and k_2 from Table V.

TABLE VI

RATE CONSTANTS FOR CURES INVOLVING 5 PARTS OF SULFUR PER 100 PARTS OF RUBBER

Curing time (min.)	k_3, 100 Gram-mole$^{-1/2}$ min.$^{-1}$
4	9.61
13	6.48
28	6.38
43	6.54
73	7.50
103	7.12
133	6.05
163	8.40
223	7.18

The rate equation for the secondary reaction can be expressed as:

$$dx/dt = k_3(b - x)^m x^n \tag{5}$$

where m and n are unknown exponents.

This equation predicts that the secondary rate should be initially zero, increase and go through a maximum, and then decrease to zero again. The difference in the calculated rates of Equations 1 and 3 when x is zero obviously will not be equal. The differences do increase, however, go through a maximum, and decrease to zero.

If Equation 5 is differentiated and set equal to zero, which is the condition for the maximum, the following relationship is obtained:

$$\frac{m + n}{n} = \frac{b}{x_{max.}} \tag{6}$$

The quantity $b/x_{max.}$ should be a constant. This was found to be true for the experiments in which the initial sulfur concentration varied. The average

value of $b/x_{max.}$ was 2.0. This indicated that m and n were equal. To determine m and n, log (dx/dt) was plotted against log $(Wb - x)x$.

$$\log (dx/dt) = m \log (b - x)x + \log k_3 \tag{7}$$

According to Equation 7, m should be the slope and log k_3 the intercept. Log (dx/dt) from all of the above experiments feel on a single straight line, whose slope was 0.69 and whose intercept indicated that the value of k_3 was 2.2×10^{-2}. m was then assigned a value of $\frac{2}{3}$. When the calculated values of (dx/dt) in Equation 5 were plotted against $[(b - x)x]^{2/3}$ straight lines which went through the origin were obtained in all cases. The slope values, which corresponded to k_3, were reasonably constant. The average value of k_3 was 2.00×10^{-2} (100 gram mole$^{-1/3}$ minute^{-1}). This information permits an equation that more accurately characterized GR-S vulcanization.

$$dx/dt = k_1 (a - y)(b - x)^2 + k_3[(b - x)x]^{2/3} \tag{8}$$

The adequacy of Equation 8 was shown when values of t were obtained from corresponding values of x by graphical integration of Equation 8. These described a curve which coincided with that obtained from experimental values.

A plot of the log of uncombined sulfur *vs.* time gave straight lines for every series of cures performed with GR-S and Hevea when mercaptobenzothiazole was used. The rate constants varied, however, with time and with change of the initial sulfur concentration.

TABLE VII

EFFECT OF SULFUR CONCENTRATION ON INITIAL MERCAPTOBENZOTHIAZOLE CONSUMPTION RATE

Percentage sulfur	Initial MBT consumption rate $\times 10^{-3}$ mole/100 g. GR-S/min.
0.5	0.196
1	1.26
3	2.69
5	5.99

In a previous section it was shown (Figures 1 to 3) that mercaptothiazole reacts initially to form the zinc mercaptide of mercaptobenzothiazole. A second reaction then takes place which depends on the sulfur concentration. These reactions take place before any sulfur has combined with the rubber. Once the sulfur-rubber reaction begins, mercaptobenzothiazole is once again consumed. The rate of this third mercaptobenzothiazole reaction is also proportional to the sulfur concentration. This information was obtained by determining the initial mercaptobenzothiazole consumption rates from the curves shown in Figures 1 to 3. The data, therefore, are only approximate. They are given in Table VII.

EFFECT OF TEMPERATURE ON COMBINING RATE OF SULFUR

Combined sulfur was measured at three temperatures for both Hevea and GR-S. The following formulation was used: polymer 100, zinc oxide 3, sulfur 3, and mercaptobenzothiazole 1. For GR-S, tare constants were calculated from Equation 4. A plot of log k_2 *vs.* the reciprocal of the absolute temperature gave a straight line. The activation energy was calculated from the slope of this line. For Hevea, the rate constant was reasonably constant at 120° C, but not at 140° and 160° C. The drop of the value of the rate constant with time at these higher temperatures presumably was due to reversion. When the

TABLE VIII

RATE CONSTANTS AND ACTIVATION ENERGIES FOR GR-S AND HEVEA

Polymer	Temp. (°C)	k_2	k^1, $\times 10^{-2}$ min.$^{-1}$	Activation energy (Kcal.)
Hevea	120	9.80	1.90	25
	140	54.4	9.40	
	160	226	35.2	
GR-S	130	1.35		37
	140	3.73		
	150	12.6		

k_2, calcd. from Equation 4. Units in 100 g. mole$^{-1/2}$ minute^{-1}.
k^1, first-order constant.

initial values of the rate constant were used and log k_2 was plotted against $1/T$, a straight line was obtained.

First-order plots of the uncombined sulfur give straight lines. If the values of k_4 obtained from these plots are used to determine the activation energy, a value identical to that obtained from the initial k_2 values of Equation 4 was obtained (Table VIII).

EFFECT OF UNSATURATION ON MERCAPTOBENZOTHIAZOLE REACTIONS

The information which has been presented up to now indicates that some initial reaction takes place between the accelerator and sulfur, which is then followed by the sulfur-rubber reaction. In order to ascertain more clearly what the early reactions were, polyisobutylene was substituted for Hevea and GR-S. It was anticipated that all reactions normally taking place with rubber would do so, but would stop at the point where the sulfur reacted with the rubber.

Samples from a compounded mixture of the following composition—polyisobutylene 100, zinc oxide 3, sulfur 3, and mercaptobenzothiazole 1—were heated at 140° C for various intervals of time and then extracted with alcohol. This treatment is the same as that given to the compounded GR-S and Hevea.

The alcohol extracts of 60- and 240-minute cures were analyzed spectroscopically in the ultraviolet region at 325mμ. Only traces of mercaptobenzothiazole were found. When these samples were dissolved in chloroform and again analyzed, a sharp absorption band was found at 325 mμ. Both mercaptobenzothiazole and its zinc mercaptide absorb at this wave length. As the zinc mercaptide is insoluble in alcohol and very soluble in chloroform, these results seem to indicate that mercaptobenzothiazole reacts completely to form the mercaptide. Samples which were heated for less than a minute, extracted with alcohol, and then dissolved in chloroform also showed almost no mercaptobenzothiazole but the presence of the mercaptide. Zinc mercaptide formation, therefore, takes place very readily.

When GR-S samples compounded in the same way as the polyisobutylene samples were cured for 60 and 240 minutes and extracted first with alcohol and then chloroform, only mercaptobenzothiazole was found. This would indicate that the mercaptide reacts readily to form another product when an unsaturated medium is present.

Evidence of zinc mercaptide formation is given by Clark, Le Tourneau, and Ball[5], who showed the presence of zinc mercaptide of mercaptobenzothiazole in x-ray patterns of vulcanizates. Additional evidence is given by Zeide and Petrov[6].

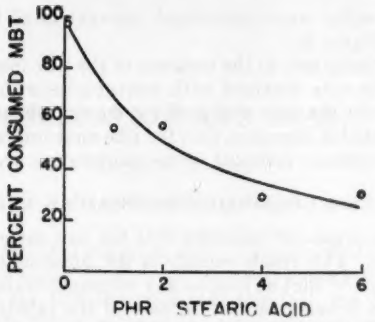


FIG. 7.—Effect of stearic acid on consumed mercaptobenzothiazole in polyisobutylene.

The effect of stearic acid on zinc mercaptide formation in polyisobutylene was determined. A standard formula of 100 parts of polyisobutylene, 3 parts of sulfur, 3 parts of zinc oxide, and 1 part of mercaptobenzothiazole was used. Stearic acid was varied over the range of 0 to 6 parts. Six to ten samples were heated at 140° C for time intervals up to 120 minutes. In all cases the amounts of consumed mercaptobenzothiazole were constant over the entire time range. Figure 7 shows that the presence of stearic acid markedly influences the amount of consumed mercaptobenzothiazole. It is believed that this is due to competitive reaction of stearic acid for zinc oxide.

VULCANIZATION WITH ZINC MERCAPTIDE OF MERCAPTOBENZOTHIAZOLE AND MERCAPTOBENZOTHIAZYL DISULFIDE

The zinc mercaptide of mercaptobenzothiazole and mercaptobenzothiazyl disulfide have been found in vulcanizates[7]. Either might be an intermediate in the curing process. The sulfur combining rates were, therefore, measured using these accelerators and compared with the rate obtained with mercaptobenzothiazole. The amounts of zinc, as the mercaptide or oxide, mercapto-

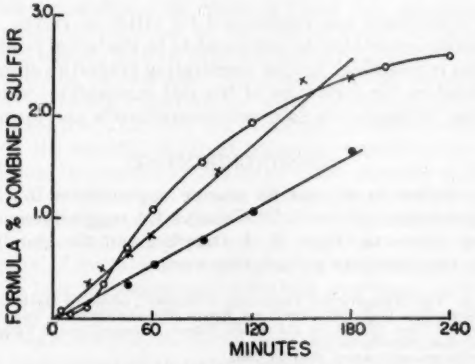


FIG. 8.—Combining rate of sulfur
Formulation. GR-S, accelerator (based on MBT) 1, zinc (as oxide and/or accelerator) 3, sulfur 3

○ MBT
× Zinc mercaptide of MBT
● MBTS

benzothiazole, and sulfur were maintained constant in all the cures. The results are shown in Figure 8.

The sulfur-combining rate in the presence of the zinc mercaptide is approximately 1.7 times the rate obtained with mercaptobenzothiazyl disulfide, and corresponds closely to the rate obtained for mercaptobenzothiazole and zinc oxide. It seems probable, therefore, that the zinc mercaptide of mercaptobenzothiazole is the intermediate involved in the acceleration process.

MECHANISM OF MERCAPTOBENZOTHIAZOLE VULCANIZATION

The information presented indicates that the zinc mercaptide is the initial product of reaction. This reacts rapidly in the presence of sulfur. Furthermore, it can be assumed that as long as any mercaptobenzothiazole is present, the zinc mercaptide is being formed because of the rapidity of this reaction. Under conditions of low mercaptobenzothiazole concentration, however, no zinc mercaptide is found except initially and near the end of the vulcanization reaction. This suggests that the zinc mercaptide of mercaptobenzothiazole is reacting as rapidly as it is formed to regenerate mercaptobenzothiazole. Since two hydrogen atoms are necessary in the conversion of the zinc mercaptide to mercaptobenzothiazole, they must come from the rubber. The rubber in its activated form (minus the hydrogen atoms) can be assumed to react with sulfur.

SUMMARY

A study has been made of the function of mercaptobenzothiazole in the vulcanization process. Radioactive sulfur[35] and mercaptobenzothiazole tagged with sulfur[35] were used for measuring the sulfur and mercaptobenzothiazole reaction rates.

The effects of variations in the zinc oxide, sulfur, and mercaptobenzothiazole concentration on the sulfur combining rates were determined. It was found that a marked induction period exists, during which the zinc mercaptide of mercaptobenzothiazole, the initial product, reacts readily with sulfur. The ratio of combined sulfur to consumed mercaptobenzothiazole is constant during the vulcanization process. A kinetic expression is given which accounts for the data.

When polyisobutylene was substituted for GR-S or Hevea, the zinc mercaptide of mercaptobenzothiazole was found to be the initial product.

A mechanism is postulated for the accelerating properties of mercaptobenzothiazole. It involves the formation of the zinc mercaptide, which reacts with sulfur and rubber to regenerate mercaptobenzothiazole and form sulfur-rubber compounds.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Carl Parks for experimental assistance and to S. D. Gehman for suggestions and encouragement. He also wishes to thank H. J. Osterhof and the Goodyear Tire and Rubber Co. for permission to publish this work.

[1] Scott and Sebrell, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., New York, 1937; Zeide and Petrov, RUBBER CHEM. & TECHNOL. 11, 97 (1938); Petrov, *J. Applied Chem.* (USSR) 16, 214 (1943); Petrov, RUBBER CHEM. & TECHNOL. 17, 56 (1944).
[2] Petrov, *J. Applied Chem* (USSR) 16, 214 (1943).
[3] Adams, H. E., private communication, May 29, 1952.
[4] Wistinghausen, *Kautschuk* 5, 57, 75 (1929); Scott and Sebrell, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., New York, 1937.
[5] Clark, Le Tourneau, and Ball, *Ind. Eng. Chem.* 35, 198 (1943).
[6] Zeide and Petrov, RUBBER CHEM. & TECHNOL. 11, 97 (1938).
[7] Zeide and Petrov, RUBBER CHEM. & TECHNOL. 11, 97 (1938); Dufraisse and Houpillart, *Rev. gen. caoutchouc* 19, 207 (1942); Clark, Le Tourneau, and Ball, *Ind. Eng. Chem.* 35, 198 (1943).

ACCELERATION AND AGING *

ADRIEN HAEHL

COMPAGNIE FRANÇAISE DES MATIÈRES COLORANTES, PARIS, FRANCE

It is a well known fact that the aging of any vulcanized rubber mixture which contains no protective agent depends on the accelerator employed for its vulcanization. Perhaps the best illustration of this fact is a comparison of the aging of two pure-gum vulcanizates of the same composition except that one was accelerated by mercaptobenzothiazole, whereas the other was accelerated by diphenylguanidine, and each was vulcanized to its optimum state of cure.

After 28 days of aging in an air oven at 70° C, the mercaptobenzothiazole vulcanizate lost 47 per cent of its original tensile strength and 40 per cent of its elongation at rupture, whereas the diphenylguanidine vulcanizate lost 87 per cent of its tensile strength and 54 per cent of its elongation at rupture.

The part played by an accelerator in the aging of vulcanized rubber containing a protective agent is a more complex phenomenon. Nevertheless, the effect is obvious to every rubber technologist. As is known, for example, the literature on commercial antioxygenic agents always gives the effects of the latter on the aging of more than one vulcanizate so as to show the effects in rubber mixtures vulcanized with different accelerators. This shows a general recognition of the fact that an accelerator has an influence on the aging of vulcanized rubber protected by an antioxygenic agent. However, the influence of accelerators on aging has not been examined in a systematic fashion.

When an investigation was made of the possible industrial use of a deactivating agent, specifically zinc mercaptobenzimidazolate[1], for protecting vulcanized rubber against aging[2], the tests were, in accord with common practice, carried out with two base mixtures, one accelerated with mercaptobenzothiazole, the other with diphenylguanidine. In choosing these two mixtures, a further purpose was to study the influence of zinc mercaptobenzimidazolate on vulcanization. It was already known that mercaptobenzimidazole itself has the serious fault of retarding vulcanization when mercaptobenzothiazole is used as accelerator and of hastening vulcanization when diphenylguanidine is the accelerator. On the contrary, the zinc salt of mercaptobenzimidazole has only a slight influence on the activity of either mercaptobenzothiazole or diphenylguanidine, which can be practically disregarded for amounts of the zinc salt below 2 per cent. However, slight as may be this influence of the zinc salt, its influence is still appreciable, and it must always be taken into account.

This led to the idea that this phenomenon might show its influence on the aging characteristics of vulcanizates protected by the zinc salt of mercaptobenzimidazole. In fact, a fundamental difference was found, as evidenced by the following facts. It is relatively easy, in the case of a vulcanizate accelerated by mercaptobenzothiazole, to obtain a considerable degree of protection against aging by combining the protective action of the zinc salt of mercapto-

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 30, No. 9, pages 654–659, September 1953.

TABLE 1

No.	Protective agent	Aging in Geer oven	Mercaptobenzothiazole: Modulus at 300% elongation (kg. per sq. cm.)	Mercaptobenzothiazole: Tensile strength (kg. per sq. cm.)	Mercaptobenzothiazole: Elongation at rupture (%)	Mercaptobenzothiazole: Rebound resilience (%)	Mercaptobenzothiazole: Hardness (Shore)	Diphenylguanidine: Modulus at 100% elongation (kg. per sq. cm.)	Diphenylguanidine: Tensile strength (kg. per sq. cm.)	Diphenylguanidine: Elongation at rupture (%)	Diphenylguanidine: Rebound resilience (%)	Diphenylguanidine: Hardness (Shore)
0	Control, with no agent	Before aging	16	152	780	79	45	18	165	720	79	48
		7 days at 70° C	22	156	675	79	50	17	125	680	77	50
		14 days at 70° C	24	151	620	78	50	16	107	610	75	48
		21 days at 70° C	26	112	540	77	50	15	48	460	72	45
		28 days at 70° C	28	80	470	76	50	14	21	330	70	45
1	Phenyl-β-napthylamine	Before aging	16	150	760	76	45	18	169	715	79	48
		7 days at 70° C	22	157	700	78	50	21	158	700	78	48
		14 days at 70° C	24	151	660	78	50	21	147	670	78	48
		21 days at 70° C	26	132	605	78	50	21	137	650	77	48
		28 days at 70° C	27	117	570	78	50	21	116	620	75	45
2	Bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl) methane	Before aging	16	155	760	75	45	19	165	730	77	45
		7 days at 70° C	21	160	700	79	50	20	163	710	77	49
		14 days at 70° C	25	160	650	79	50	21	163	690	76	50
		21 days at 70° C	26	128	530	79	51	21	161	680	75	50
		28 days at 70° C	28	79	480	79	52	21	149	660	74	49
3	Zinc salt of mercapto-benzimidazole	Before aging	13	131	780	73	44	21	172	715	80	50
		7 days at 70° C	19	161	750	74	48	23	135	680	80	50
		14 days at 70° C	20	157	710	74	48	24	117	590	74	50
		21 days at 70° C	21	146	690	74	48	24	96	550	73	50
		28 days at 70° C	21	140	670	74	48	25	78	520	71	48

benzimidazole with that of a "true" antioxygenic agent. On the contrary, when the accelerator is diphenylguanidine, the synergetic effects of the protection by the same combination of protective agents are slight or practically negligible.

CLASSIFICATION OF PROTECTIVE AGENTS IN RELATION TO THE ACCELERATOR

Taking into account the poor aging of vulcanizates accelerated by diphenylguanidine, an effort was made, first of all, to find a protective agent which is particularly effective with diphenylguanidine. As a means to this end, products now available have been classified on the basis of their value with diphenylguanidine.

To make such a classification successfully, base rubber mixtures used in earlier work were used. These mixtures are recorded below. To distinguish

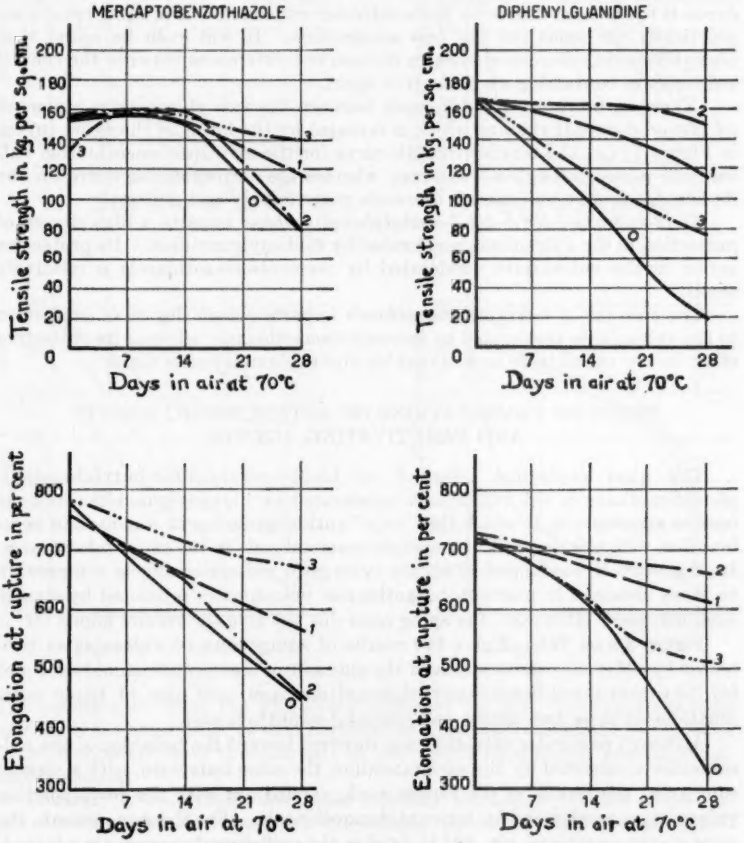


FIG. 1

particularly sharply between the behavior of different vulcanizates, 70° C was chosen as the temperature for aging, instead of the 80° C used in the previous investigation.

The recipe used in the experiments was (in parts by weight) as follows: smoked-sheet rubber 100, sulfur 3, accelerator 1, protective agent 0 and 2, stearic acid 1, zinc oxide 5.

Vulcanization.—The mixtures accelerated by mercaptobenzothiazole were vulcanized for 20 minutes at 143° C; those accelerated by diphenylguanidine were vulcanized for 40 minutes at 143° C.

Table 1 and Figure 1 show some aging effects obtained with three protective agents, now on the market, the behavior of which reveals characteristic differences in their effects with the different accelerators.

The important differences brought out by the tests may be summarized as follows.

Phenyl-β-naphthylamine is a protective agent, the effectiveness of which depends to the least degree on the accelerator employed. The aging results are practically the same for the two accelerators. It will even be noted that phenyl-β-naphthylamine eradicates the marked differences between the control vulcanizates containing no protective agent.

There is, however, one difference between the two vulcanizates protected by phenyl-β-naphthylamine which is revealed by the forms of the aging curves in Figure 1; *i.e.*, the tensile strength curve for the mercaptobenzothiazole vulcanizate passes through a maximum, whereas the corresponding curve for the diphenylguanidine vulcanizate descends progressively and uniformly.

Bis(2-hydroxy-3-tert-butyl-5-methylphenyl)methane imparts a high degree of protection to the vulcanizate accelerated by diphenylguanidine. Its protective action in the vulcanizate accelerated by mercaptobenzothiazole is relatively small.

The *zinc salt of mercaptobenzimidazole* imparts a high degree of protection to the vulcanizate accelerated by mercaptobenzothiazole, whereas its protective effect in the vulcanizate accelerated by diphenylguanidine is slight.

STUDY OF COMBINATIONS OF ANTIOXYGENIC AGENTS AND DEACTIVATING AGENTS

The good protection afforded by bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane in the vulcanizate accelerated by diphenylguanidine induced further experiments, in which this "true" antioxygenic agent was used in combination with the zinc salt of mercaptobenzimidazole in the same vulcanizates. In this way it was hoped to obtain synergetic protective effects comparable to those obtained in mercaptobenzothiazole vulcanizates protected by similar combinations. However, the aging tests did not give the results hoped for.

Figure 2 and Table 2 give the results of aging tests of vulcanizates protected by different combinations of the zinc salt of mercaptobenzimidazole and bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane, and also of triple combinations of these two agents and phenyl-β-naphthylamine.

Although particular attention was directed toward the behavior of the vulcanizates accelerated by diphenylguanidine, the same tests were, with a view to comparing the results of the earlier work, carried out with the corresponding vulcanizates accelerated by mercaptobenzothiazole. For the same reason, the more severe conditions, *viz.*, 80° C, used in the earlier work were again adopted.

Diphenylguanidine.—The aging of vulcanizates accelerated by diphenylguanidine present the simplest case. The aging curves of the control mixture containing no protective agent descend uniformly, and their slopes are considerable for aging at 70° C and steep for aging at 80° C. The addition of a protective agent does not change the form of the curve but does reduce its slope.

Bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane has considerable protective effect in the aging of the vulcanizate accelerated by diphenylguanidine.

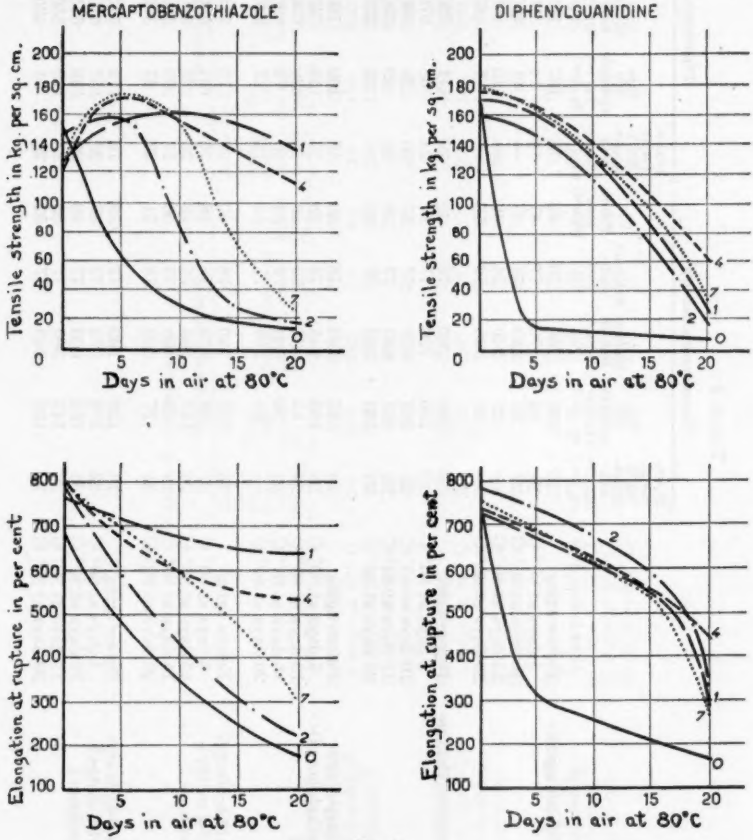


FIG. 2

The results show that the protection conferred by this "true" antioxygenic agent is of the same order as that imparted to the same vulcanizate by the most active combinations of the zinc salt of mercaptobenzimidazole and phenyl-β-naphthylamine.

Contrary to what might have been expected, the added presence of the zinc salt of mercaptobenzimidazole in a vulcanizate containing bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane does not have any notable effect. The very

TABLE 2

No.	Protective agent	Aging in Geer oven	Mercaptobenzothiazole					Diphenylguanidine				
			Modulus at 300% elongation (kg. per sq. cm.)	Tensile strength (kg. per sq. cm.)	Elongation at rupture (%)	Rebound resilience (%)	Hardness (Shore)	Modulus at 300% elongation (kg. per sq. cm.)	Tensile strength (kg. per sq. cm.)	Elongation at rupture (%)	Rebound resilience (%)	Hardness (Shore)
0	Control without agent	Before aging	15	151	790	79	42	18	167	730	81	43
		5 days at 80° C	21	65	470	77	47	14	14	300	76	40
		10 days at 80° C	27	31	340	75	48	—	11	260	70	36
		15 days at 80° C	—	21	240	74	49	—	10	210	66	35
		20 days at 80° C	—	16	190	73	50	—	7	161	61	34
1	Phenyl-β-naphthylamine 1, zinc 2	Before aging	13	130	760	76	40	20	171	720	81	43
		5 days at 80° C	19	156	720	77	47	24	165	670	82	45
		10 days at 80° C	21	163	670	77	47	26	129	600	79	46
		15 days at 80° C	22	155	660	77	48	26	90	550	78	47
		20 days at 80° C	23	140	630	77	49	—	22	275	74	44
2	Bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-methane 3	Before aging	14	146	780	78	40	15	160	790	82	38
		5 days at 80° C	24	160	645	79	48	17	149	740	79	42
		10 days at 80° C	29	85	435	79	48	16	129	690	76	40
		15 days at 80° C	30	30	300	79	50	16	73	590	76	39
		20 days at 80° C	—	21	210	77	51	15	17	320	71	37
3	Zinc 1, bis(2-hydroxy-3-*tert*-butyl-5-methyl-phenyl)-methane 1	Before aging	13	137	790	78	40	19	175	715	83	42
		5 days at 80° C	22	168	670	78	48	26	151	680	81	45
		10 days at 80° C	26	137	585	78	48	26	135	610	79	46
		15 days at 80° C	28	85	460	78	50	27	109	560	78	46
		20 days at 80° C	31	27	330	78	51	27	27	300	76	46
4	Zinc 2, bis(2-hydroxy-3-*tert*-butyl-5-methyl-phenyl) methane 1	Before aging	13	126	790	77	39	19	175	740	82	43
		5 days at 80° C	22	176	670	77	47	26	157	670	81	45
		10 days at 80° C	25	164	600	77	48	26	138	615	79	46
		15 days at 80° C	26	145	560	77	50	27	118	550	78	46
		20 days at 80° C	27	128	540	77	52	28	61	430	75	46

TABLE 2—(*Continued*)

No.	Protective agent	Aging in G. er oven	Mercaptobenzothiazole					Diphenylguanidine				
			Modulus at 300% elongation (kg. per sq. cm.)	Tensile strength (kg. per sq. cm.)	Elongation at rupture (%)	Rebound resilience (%)	Hardness (Shore)	Modulus at 300% elongation (kg. per sq. cm.)	Tensile strength (kg. per sq. cm.)	Elongation at rupture (%)	Rebound resilience (%)	Hardness (Shore)
5	Zinc 1, bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-methane 2	Before aging	14	137	800	78	40	18	173	750	82	45
		5 days at 80° C	24	176	685	79	48	25	139	660	81	45
		10 days at 80° C	28	141	595	79	49	26	123	509	79	45
		15 days at 80° C	29	70	470	79	50	27	83	430	78	45
		20 days at 80° C	30	46	360	78	51	27	28	315	75	45
6	Phenyl-β-naphthylamine 0.5, zinc 0.5, bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-methane 0.5	Before aging	14	135	780	78	40	18	178	740	84	45
		5 days at 80° C	23	172	680	78	47	22	144	690	80	45
		10 days at 80° C	26	164	630	78	48	23	116	620	78	45
		15 days at 80° C	28	75	470	78	49	23	63	450	76	45
		20 days at 80° C	31	31	300	78	51	—	14	220	72	45
7	Phenyl-β-naphthylamine 1, zinc 0.5, bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)-methane 1	Before aging	13	130	790	79	40	19	180	760	83	43
		5 days at 80° C	22	178	710	79	46	23	163	690	81	45
		10 days at 80° C	25	162	640	79	47	25	131	610	79	45
		15 days at 80° C	27	66	470	79	49	26	98	520	78	45
		20 days at 80° C	30	31	310	78	51	—	21	260	75	45

best improvement in resistance to aging, which was attained by 2 parts of the zinc salt of mercaptobenzimidazole plus 1 part of "true" antioxygenic agent, is too small for it to be regarded as a synergetic effect, particularly since the improvement is in the region of the greatest spread of the aging values[3]. The addition of phenyl-β-naphthylamine to this double combination of protective agents does not improve the resistance to aging; in fact, the results with this triple combination indicate poorer aging.

In no case is the improvement of aging of the diphenylguanidine vulcanizate by combinations of protective agents comparable to the improvement attained in the earlier work with vulcanizates accelerated by mercaptobenzothiazole.

Mercaptobenzothiazole.—The mechanism of protection of vulcanizates accelerated by mercaptobenzothiazole is much more complex. It is known that these vulcanizates, even when vulcanized to their optimum cure, show at the beginning of aging a further increase of tensile strength. In other words, as aging progresses, a new maximum tensile strength is passed through, which is greater than the optimum value on the curve showing tensile strength as a function of the time of vulcanization. It may be said that the vulcanizate has in reserve a maximum tensile strength which is higher than its original maximum strength and which comes to light only in the earlier stage of aging[4]. There would seem to be a certain relation between this characteristic effect and the effect of the zinc salt of mercaptobenzimidazole, although nothing definite can be said in view of the fact that no tests have been made with other accelerators which show the same phenomenon.

It was established in the earlier work that the zinc salt of mercaptobenzimidazole acts from the beginning of vulcanization on the mechanical properties of the vulcanized rubber; there is a decrease of tensile strength, decrease of modulus, decrease of hardness, decrease of rebound resilience, and increase of elongation at rupture. Of particular interest is the fact that the mechanical properties for the optimum state of cure are not the same for vulcanizates containing and not containing the zinc salt. This influence of the zinc salt of mercaptobenzimidazole on the mechanical properties of vulcanizates accelerated by mercaptobenzothiazole shows that this zinc salt must, during vulcanization, cause changes in the structure of the vulcanizate. However, this impairment of the mechanical properties is fully compensated for during aging; in fact, the tensile strength, though lower in the beginning, passes during aging through a maximum value which is much higher than the optimum tensile strength of the corresponding vulcanizate containing no zinc salt. At the same time, the optimum point of the aging curve is shifted by the zinc salt of mercaptobenzimidazole toward longer times, and analogously the depression of the curve representing a degradation of structure is shifted toward longer times. The resistance to aging is thus considerably increased by the action of the zinc salt of mercaptobenzimidazole alone.

In addition, if a "true" antioxygenic agent also is present in a vulcanizate thus stabilized by the zinc salt of mercaptobenzimidazole, the "true" antioxygenic effect, which is entirely different from that of the zinc salt, is added to the effect of the latter. In this way, pronounced synergetic effects are attained.

From this viewpoint, bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane exhibits remarkable additive power of protection. This particular "true" antioxygenic agent has only a relatively small protective action on the aging of vulcanizates accelerated by mercaptobenzothiazole, but, by combination with the stabilizing action of the zinc salt of mercaptobenzimidazole, excellent protection is obtained. The effect approaches, in fact, that obtained with a combina-

tion of the zinc salt and phenyl-β-naphthylamine. Under these conditions, phenyl-β-naphthylamine shows itself to be a more effective "true" antioxygenic agent than bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane. An examination of the results shows: (1) that the possibility of protecting a vulcanizate against aging depends primarily on the nature of the accelerator and not so much on the protective agent employed; and (2) that the mechanism of aging, particularly when protective agents are present, of a vulcanizate accelerated by mercaptobenzothiazole, is not the same as that of a vulcanizate accelerated by diphenylguanidine.

THEORETICAL CONCLUSIONS

The experiments described in the present work show that the mechanism of the protection of rubber against aging depends on the particular accelerator employed for vulcanization. As a consequence, it may be that it is impossible to formulate any general theory which applied to both protective agents and accelerators.

In the case of vulcanizates accelerated by diphenylguanidine, there is no conclusive evidence of a synergetic effect between the action of "true" antioxygenic agents and that of the zinc salt of mercaptobenzimidazole. The improvements attained by the use of a combination of these two types of protective agents are, in fact, very small and do not exceed the range of variation of the aging tests. However, since it has been shown that the zinc salt alone has practically no protective action in vulcanizates accelerated by diphenylguanidine, the only conclusion that can be drawn at this time is that these two ingredients are in some way incompatible with each other. Further experiments would have to be carried out to throw further light on the problem, and to determine the extent to which protection by the deactivation effect is attainable in vulcanizates accelerated by basic compounds.

In the case of vulcanizates accelerated with mercaptobenzothiazole, the zinc salt of mercaptobenzimidazole changes the mechanical properties and must, therefore, have some sort of effect on the structure of the vulcanizate. If this structure is different from that of the corresponding vulcanizate containing only mercaptobenzothiazole, it is quite natural that the aging phenomena should differ, and, in fact, experiments show that the presence of the zinc salt of mercaptobenzimidazole greatly improves the aging properties.

All this seems to indicate that the structure of a vulcanizate containing the zinc salt is more resistant to aging than is that of the corresponding vulcanizate containing mercaptobenzothiazole but not the zinc salt. The effect, then, of the deactivating agent would be, not the deactivation of peroxides formed during aging, but a process which may be regarded as some sort of stabilization of the structure from the very beginning of vulcanization. From this viewpoint, the effect would be that of a special form of acceleration; in fact, this analogy between the action of deactivating agents and accelerators has already been pointed out by Le Foll[6] in connection with experiments on relaxation.

The "true" antioxygenic effect, which is entirely different from the stabilizing effect, can add to the latter during aging, and the combination of the two protective effects serves to explain the marked synergetic effects observed with vulcanizates accelerated by mercaptobenzothiazole, stabilized by the zinc salt of mercaptobenzimidazole, and protected by a "true" antioxygenic agent.

If this hypothesis is correct, it might be conceived that, in the case of diphenylguanidine, the mechanism of acceleration does not favor stabilization by the zinc salt. This would, in turn, explain the absence of any protective effect

of the zinc salt by itself and the absence of any synergetic effect when a "true" antioxygenic agent is present. In this case, to improve the aging properties of these vulcanizates, new types of deactivating agents would have to be found, the stabilizing effect of which would be compatible with the basic acceleration.

PRACTICAL CONCLUSIONS

The accelerator employed for vulcanization plays a fundamental role in the aging of vulcanized rubber, whether or not the latter contains a protective agent against aging.

When the maximum resistance to aging is sought for, it is advantageous to use mercaptobenzothiazole as the accelerator of vulcanization. In a vulcanizate accelerated in this way, protection against aging by marked synergetic effects is obtained by a mixture of the zinc salt of mercaptobenzimidazole and a "true" antioxygenic agent.

Vulcanizates accelerated by diphenylguanidine have, in general, relatively poor resistance to aging. When employed alone, bis(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane has proved itself to be a very satisfactory protective agent. However, its effectiveness is not appreciably increased by the joint use of the zinc salt of mercaptobenzimidazole. The very best aging obtained with vulcanizates accelerated by diphenylguanidine is in all cases poorer than the aging of corresponding vulcanizates accelerated by mercaptobenzothiazole.

SUMMARY

In a study of the protection of vulcanized rubber against aging by combinations of the zinc salt of mercaptobenzimidazole and "true" antioxygenic agents, it has been found that such combinations have a synergetic effect of considerable magnitude in the protection of vulcanizates which are accelerated by mercaptobenzothiazole. On the other hand, in the case of vulcanizates accelerated by diphenylguanidine, the effect is slight or even negligible.

On the assumption, therefore, that the nature of the accelerator has a great influence on the effectiveness of the protective agents, the latter were classified with respect to the accelerators used. In this way it was established that bis-(2-hydroxy-3-*tert*-butyl-5-methylphenyl)methane, when employed alone is by far the best protective agent against the aging of vulcanized rubber accelerated by diphenylguanidine.

In addition by combining this "true" antioxygenic agent with the zinc salt of mercaptobenzimidazole it was found that only slightly greater protection can be attained than is possible by the antioxygenic agent alone. Consequently in this case one should not speak of a synergetic effect.

The experiments lead quite definitely to the conclusion that the mechanism of protection against aging when a deactivating agent is present depends upon whether the accelerator employed is mercaptobenzothiazole or diphenylguanidine.

REFERENCES

[1] Le Bras, *Rev. gén. caoutchouc* 21, 3 (1944); Le Bras and Viger, *Rev. gén. caoutchouc* 21, 89 (1944).
[2] Haehl, *Rev. gén. caoutchouc* 26, 563, 619 (1949).
[3] Experiments have shown that the aging curves derived from data obtained at 80° C have regular slopes to the points corresponding to a tensile strength of 100–120 kg. per sq. cm. and an elongation at rupture of 450–500 per cent. The curves then descend abruptly, apparently corresponding to rapid molecular degradation of the vulcanizates. In this region, the tensile strength decreases rapidly to 20–30 kg. per sq. cm. and the elongation at rupture to 250–300 per cent. In this transition and degradation zone, there is considerable variation in the measurements of the mechanical properties. As evidenced by the reduced slopes of the aging curves, the protective agent prolongs the point of time in the aging process at which molecular degradation begins.
[4] For information on this subject, see Judeinstein, *Rev. gén. caoutchouc* 26, 273 (1949).
[5] In these experiments, the optimum tensile strength on aging of some vulcanizates was found to exceed by 50 per cent the optimum tensile strength attained at any state of cure.
[6] Le Foll, *Rev. gén. caoutchouc* 30, 559 (1953).

A STUDY OF THE MECHANISM OF THE DEACTIVATION EFFECT *

JACQUES LE FOLL

FRENCH RUBBER INSTITUTE, PARIS, FRANCE

INTRODUCTION

A preceding paper[1] described a study of a number of chemical derivatives and led to the conclusion that the deactivation effect must be attributed to the presence of a thiol group which is rendered more or less active by a cyclic structure and by neighboring hetero atoms. There remained the problem of determining the mechanism of this specific protective effect and in what way it differs from the classic antioxygenic effect.

Before entering into a discussion of the theories which have been advanced concerning the mechanism of the deactivation effect, it seemed well to review briefly the theory of the antioxygenic effect.

THEORY OF THE ANTIOXYGENIC EFFECT

In 1923, Moureu and Dufraisse put forward a theory[2] which was later modified by Dufraisse himself. This theory is too well known to warrant its being described in detail at this point, and the following scheme will suffice to show its essential points:

$$A + O_2 \longrightarrow A[O_2] \tag{1}$$

(autoxidation to a primary peroxide.

$$A[O_2] + B \longrightarrow A[O_2]B \tag{2}$$

$$A[O_2]B \begin{cases} \nearrow A + B + O_2 \text{ (negative catalysis)} \\ \searrow AO_2 + B \text{ (positive catalysis)} \end{cases} \tag{3}$$

In the first case, *B* acts as an antioxygenic agent, in the second case, it acts as a prooxygenic agent.

PRINCIPAL THEORIES OF THE DEACTIVATION EFFECT

How can the action of an inhibitor *C*, *e.g.*, mercaptobenzimidazole, which is an efficient protective agent against aging, yet has hardly any influence on the rate of oxidation, be reconciled with the theories described above? Experiments have shown that, in this case, rubber can tolerate relatively large proportions of oxygen without showing any appreciable indications of deterioration. It may, therefore, be assumed, in accord with the view of Le Bras[4], that since this inhibitor does not obstruct the combination of oxygen, it in some way deactivates the peroxides as fast as they are formed by transforming them into

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 30, No. 8, pages 559–562, August 1953. This paper is a condensation of a thesis presented at Paris, February 2, 1952, in anticipation of the degree of Doctor of Engineering.

simple oxides which are insufficiently reactive to degrade the rubber molecule. In this case, the general scheme of reactions would be as follows:

$$A + O_2 \longrightarrow A[O_2] \text{ (autoxidation to primary peroxide)} \quad (1)$$

$$A[O_2] + C \longrightarrow A[O_2]C \quad (2)$$

$$\left.\begin{array}{l} A[O_2]C \longrightarrow C + AO_2 \text{ (stable oxide)} \\ \text{or} \\ A[O_2]C + A \longrightarrow C + 2AO \text{ (stable oxide)} \end{array}\right\} \text{deactivation effect} \quad (3)$$

The deactivating agent therefore orients the oxidation process toward reactions which involve fixation, without scission, of oxygen on the rubber molecule.

It would seem, *a priori*, easy to verify these hypotheses by determining the peroxidic oxygen content and the molecular weight of rubber protected by a deactivating agent. But, because of its insolubility in solvents, vulcanized rubber does not lend itself to such determinations. For this reason, Le Bras and Salvetti[5] decided to have recourse to unvulcanized rubber. Unfortunately, all experiments with the latter were fruitless, because it was found that there is no appreciable deactivation effect with unvulcanized rubber.

This means that the deactivation effect is specific to vulcanized rubber, and therefore the latter is the only form of rubber which is adapted to this type of investigation. Consequently, there is no point in studying by purely chemical methods the effects of oxidation. The only experimental method which can be used is to study the differences of behavior, by measurements of aging effects or of oxidizability, of vulcanizates protected on the one hand by an antioxygenic agent or, on the other, by a deactivating agent.

In view of all this, the work described in the present paper was directed to a study of two phenomena:

(1) analysis of the gases which are evolved during oxidation in a current of oxygen, and
(2) changes of modulus and of swelling in solvents during oxidative aging.

Unfortunately neither of these methods brought out any characteristic differences between the effects of antioxygenic agents and of deactivating agents.

However, the problem of aging can be approached from a different point of view by utilizing certain experimental results recently obtained by Tobolsky, Prettyman, and Dillon[6].

RELAXATION TESTS

By relaxation tests, the principle of which is described below, these investigators were able to demonstrate that oxygen has two distinctly different effects on rubberlike polymers, *viz.*, on the one hand, scission of the chains, and, on the other hand, the formation of intermolecular bonds.

This concept serves to explain why some vulcanizates become very soft during aging, whereas other vulcanizates harden progressively. In the first case, chain scission is the predominant reaction; in the second case, the phenomenon of intermolecular bonding is the predominant effect.

When measurements are made of the stress modulus of a vulcanizate aged in an oven for increasing periods of time, the measurements actually indicate the net result of chain scission and of intermolecular bonding, which proceed

simultaneously during accelerated aging. On the contrary, relaxation measurements, by which changes of stress at constant elongation during accelerated aging are determined at increasing periods of aging, indicate only the phenomenon of chain scission. Actually, according to the theory of Tobolsky and his coworkers, any intermolecular bridges which are formed at the elongated points do not contribute to the total stress. Measurements of the relaxation of natural and synthetic rubber vulcanizates have verified these hypotheses, and we shall see later that the latter make it possible to interpret certain facts which are, *a priori*, rather surprising.

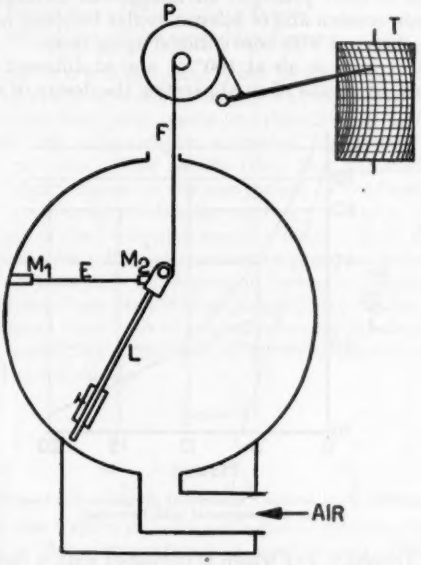


FIG. 1.—Diagrammatic scheme of the apparatus for making relaxation measurements in air at 100° C.

E Rubber test-specimen
M_1 Fixed clamp
M_2 Movable clamp
L Lever arm
F Transmission wire
T Rotating recording drum

According to the experiments of Tobolsky and his coworkers, the relaxation effect of both natural rubber and synthetic rubber vulcanizates comprises two phases: (1) an initial rapid decrease of the stress, and (2) subsequent relatively slow decrease of the stress. It will be shown that experiments by the present author confirm in every way the results obtained by Tobolsky and his coworkers.

First of all, the bonds between the long molecular chains are either primary chemical bonds (valence bonds) or bonds of a secondary nature (van der Waals forces). It can, then, be assumed that the initial rapid decrease of stress is the result of the relaxation of the more fragile secondary bonds, and that the subsequent slower decrease of stress depends on scission, either at any point of the chains or at the intermolecular bonds which are formed during vulcanization.

This point of view is supported by the fact that the initial phase of relaxation does not depend on the composition of the surrounding medium, whereas the second phase of the relaxation takes place only if the surrounding medium contains oxygen. This demonstrates also that oxygen is responsible for the scission effect which is observed.

Thus it is possible, by means of relaxation tests, to follow the phenomena involved in the oxidative aging of rubber-like substances with a precision and reproducibility much more satisfactory than the precision and reproducibility of the classic methods of studying aging. In addition, relaxation tests make it possible—and this is their principal advantage—to distinguish between the phenomena of chain scission and of intermolecular bonding, only the combined effect of which is observed with conventional aging tests.

Tests were carried out in air at 100° C, and at different elongations from 150 to 300 per cent, by means of an apparatus, the design of which is based on

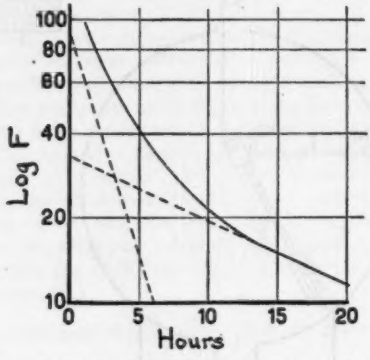


FIG. 2.—Logarithm of the tension F at constant elongation as a function of the time during the progress of oxidative aging.

the apparatus of Tobolsky, but which is furnished with a device by which the results can be recorded graphically and continuously. This new apparatus is shown schematically in Figure 1.

It may be assumed, in conformity with the theories of Tobolsky, that the immediate tension F which is recorded is the sum of two terms which represent, respectively, the tension, F_1, due to valence forces, the other F_1, due to van der Waals forces:

$$F = F_1 + F_2$$

The experimental results obtained show that, during relaxation, both F_1 and F_2 decrease as an exponential function of time:

$$F_1 = (F_1)_0 \times 10^{-\alpha t}$$
$$F_2 = (F_2)_0 \times 10^{-\beta t}$$

where t represents the time variable. Hence:

$$\log F_1 = \log (F_1)_0 - \alpha t$$
$$\log F_2 = \log (F_2)_2 - \beta t$$

The logarithms of the partial tensions are, consequently, linear functions of the time. This can be shown graphically by plotting the logarithms of the tension F as a function of time (see Figure 2). The curves in Figure 2 make it possible to calculate the values of the α and β coefficients. From a practical point of view, the results should not be expressed in terms of the α and β values, but rather by the values of the times of relaxation of the primary and secondary forces.

The times of relaxation may be expressed as the time (in hours) for the tension to fall to one-half its original value:

t_1 the time of relaxation of the primary forces.
t_2 the time of relaxation of the secondary forces.

Knowing the values of α and β, t_1 and t_2 can be easily calculated.

This method of study of oxidative aging was made use of to compare the protective effects of antioxygenic agents and deactivating agents. The experiments were carried out with samples elongated to different degrees, ranging from 175 to 280 per cent. The results show that the coefficients t_1 and t_2 depend to only a slight degree on the elongation, in conformity with the data already reported by Tobolsky. On the contrary, t_1 and t_2 depend to a large extent on the nature of the protective agent. Table 1 gives the t_1 and t_2 values for vulcanizates containing different protective agents and elongated to 280 per cent. Here T is a vulcanizate containing no protective agent, A the same base vulcanizate containing 2 per cent of phenyl-β-naphthylamine, D the same base vulcanizate containing 2 per cent of mercaptobenzimidazole, and AD the same base vulcanizate containing 1 per cent of phenyl-β-naphthylamine and 1 per cent of mercaptobenzimidazole.

TABLE 1

	T	A	D	AD
t_1 (hours)	13	43	24	55
t_2 (hours)	1.9	1.8	1.5	1.4

The data in Table 1 show that the protective agents act for the most part on the relaxation of the primary forces (t_2 coefficients). This is further confirmation of the general theories already advanced.

By making relaxation measurements at constant elongation, it is possible to distinguish the relaxation of the primary forces from the relaxation of the secondary forces, which proceed simultaneously during aging, and to calculate the corresponding values of the times of relaxation.

The relaxation of the secondary forces, which are an indication of slippage of the molecular chains relative to one another when the tension exceeds the van der Waals forces, can take place only in samples maintained under tension. Consequently, in conventional aging tests, whether accelerated or not, no changes of the secondary forces are observed, but only changes of the primary forces (chemical or valence bonds).

It appears, then, that the two methods already described, which we shall call the *continuous method* for relaxation tests under constant tension and the *discontinuous method* for measurements of the changes of modulus during normal aging, do not give parallel results, since the same factors do not play a part in the two cases. Results by the two methods are logically comparable only if, in the case of the continuous method, the component representing the relaxation of the secondary forces is disregarded. This led us to calculate the changes of a

factor F', which can be easily done by increasing the instantaneous value of F_1 (strength of the primary bond) by the initial value, $(F_2)_0$, of F_2 (strength of the secondary bond): $F' = F_1 + (F_2)_0$.

This calculation is very easy if the curves recorded by the continuous method, are utilized for this purpose. The principles of interpreting the results of this method have been described earlier in this paper.

Table 2 records the changes of F' during the aging of the T, A, D, and AD vulcanizates. These changes also are shown graphically by the unbroken curves in Figure 3. Figure 3 shows also, as broken curves, the changes of modulus of the same four vulcanizates elongated at 280 per cent.

To interpret correctly the curves in Figure 3, it must be remembered that, in conformity with the theories of Tobolsky, the broken curves, plotted from data obtained by the discontinuous method, record the changes of the combined result of the phenomena of scission and of intermolecular bonding, while the unbroken curves, plotted from data obtained by the continuous method, indicate only the scission phenomenon.

TABLE 2

		Time of aging at 100° C at 280% elongation (in hours)			
		0	5	10	15
T	F'	118	110	104	100
	Percentage change of F'	0	−7	−12	−16
A	F'	135	130	122	122
	Percentage change of F'	0	−4	−6.5	−10
D	F'	122	115	109	103
	Percentage change of F'	0	−6	−11	−15.5
AD	F'	72	69	66	63
	Percentage change of F'	0	−2.5	−5	−7.5

For the control vulcanizate, T, containing no protective agent, the differences obtained by the two methods of aging are relatively small; the two curves of the data obtained by the discontinuous and continuous methods follow almost the same course. This would lead to the conclusion that the phenomena of intermolecular bonding play no significant role.

For the vulcanizate containing phenyl-β-naphthylamine, the continuous relaxation is greater than the discontinuous relaxation, but the differences are not of any considerable magnitude. Here, too, the phenomena of intermolecular bonding are practically negligible.

For the vulcanizate containing mercaptobenzimidazole, the spread between the two curves is relatively great. The continuous relaxation is identical to that of the control vulcanizate containing no protective agent, whereas the discontinuous relaxation is much less than that of the control vulcanizate. It would seem therefore that, in this case, the phenomena of intermolecular bonding play a major part during the aging process.

The same effects are evident in the case of the vulcanizate containing both phenyl-β-naphthylamine and mercaptobenzimidazole.

These experiments are certainly not sufficiently comprehensive to make possible any definitive conclusions. To reach any such conclusions, the experiments would have to be completed with an apparatus which would measure

the relaxation more sensitively and by a study of the influence on the relaxation phenomena of various factors, such as the elongation and temperature.

However, the results do throw light on one aspect of the deactivation effect which has not been realized heretofore and a study of which seems to be capable of giving fruitful results.

Antioxygenic agents seem to obstruct any scission reactions which are brought about through the agency of oxygen, either at any point along the chains or at the intermolecular bridges. On the contrary, deactivating agents,

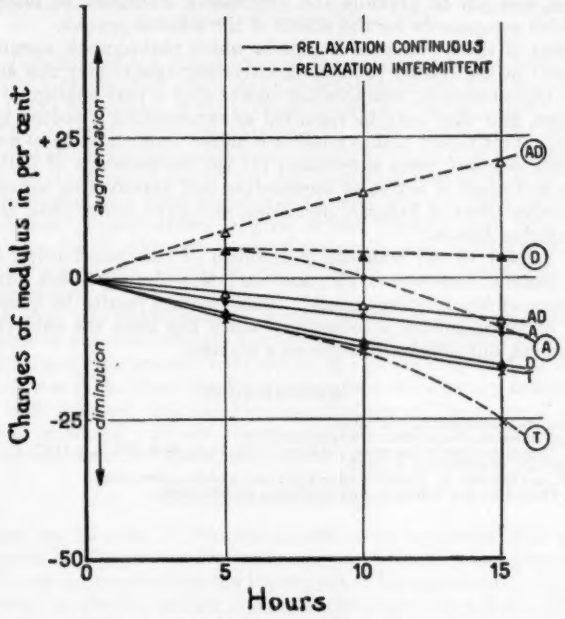


FIG. 3.—Changes of $F' = F_1 + (F_2)_0$ (unbroken curves) and of the modulus at 280 per cent (broken curves) during the progress of oxidative aging of four mixtures protected in different ways.

T Control vulcanizate containing no protective agent
A Vulcanizate containing an antioxygenic agent
D Vulcanizate containing a deactivating agent
AD Vulcanizate containing both an antioxygenic agent and a deactivating agent

though protecting against oxidative aging, seem not to prevent scission taking place but to promote the formation of intermolecular bonds. This would explain the considerably less damaging effect of absorbed oxygen in vulcanized rubber containing a deactivating agent.

CONCLUSIONS

The only method by which significant differences between the effects of antioxygenic agents and deactivating agents can be detected has been found to be a study of relaxation phenomena. An investigation by this method has also furnished further support to the theories of Tobolsky and his coworkers.

The changes which take place during aging in the physical properties of vulcanized rubber are the result of two independent phenomena which occur simultaneously: (1) chain scission, and (2) formation of intermolecular bonds.

As far as the aging of vulcanizates of natural rubber under normal conditions, *e.g.*, socalled natural aging, is concerned, the chief phenomenon involved is scission of the chain molecules.

In principle, therefore, there are two methods for combatting the deterioration of rubber on aging: (1) to impede chain scission by obstructing the fixation of oxygen, and (2) to promote the progressive formation of intermolecular bonds which compensate for the effects of the scission process.

The first of these processes is that in which antioxygenic agents play the active part; in the second process, deactivating agents play the active part.

From this viewpoint, deactivating agents play a part analogous to that of accelerators, and they may be regarded as representing a special type of acceleration. This theory makes possible a better understanding of a number of facts which, *a priori*, seem surprising: (1) the relationships of both chemical structure and mode of action of accelerators and deactivating agents, and (2) the protective effect of litharge, peroxides, and nitro compounds, all of which are vulcanizing agents.

With respect to the intimate mechanism of the deactivating effect, one question remains unanswered, *viz.*, how are intermolecular bonds formed under the influence of deactivating agents? This question recalls the question of the function of vulcanization accelerators, which has been the subject of many investigations, but which still remains a mystery.

REFERENCES

[1] Le Foll, *Rev. gén. caoutchouc* **29**, 114 (1952).
[2] Moureu and Dufraisse, *Compt. rend.* **176**, 624 (1923).
[3] Dufraisse, "Traité de Chimie Organique", Masson & Cie, Paris, **1936**, Vol. 2, p. 1147.
[4] Le Bras, *Rev. gén. caoutchouc* **21**, 3 (1944).
[5] Le Bras, J., and Salvetti, A., French Rubber Inst., unpublished experiments.
[6] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944).

EQUILIBRIUM BETWEEN RUBBER AND ALCOHOL–BENZENE SOLUTIONS *

G. L. STAROBINETS AND V. S. KOMAROV

PHYSICS AND COLLOID CHEMISTRY LABORATORIES, V. I. LENIN WHITE RUSSIAN GOVERNMENT UNIVERSITY, MINSK, USSR

A careful study of the distribution of the components of a binary solution between the high-polymer phase and the solution phase is of the utmost importance in the derivation of the thermodynamics of ternary systems comprising a high polymer-binary liquid mixture[1]. The phenomenon of selective absorption of one of the components of a binary solution by a high polymer has been noted in a number of works[2], but the quantitative data reported to date on this question refer to a small number of systems and are quite insufficient for any theoretical generalizations. More or less detailed data exist for polystyrene-binary liquid systems[3], but in these works, too, no attention has been paid to dilute solutions, which, as will be shown in the present study, are of great significance.

In this work, the distribution of the components of binary solutions of normal alcohols in benzene between the solution and vulcanized natural rubber was investigated, with special attention to the dilute solutions. The purpose of the work was (1) to show the distribution between a binary solution and an insoluble high polymer, and also the general shape of the curve of isothermic equilibrium, in accord with the theories of Konovalov[4], and (2) to study the relation between selective absorption and the structure of solutions.

EXPERIMENTAL PART

Swelling was effected in the vapor phase in an apparatus with a mercury seal, depicted in Figure 1. The components of the solution were added by means of a curved pipette into the lower part of the apparatus. The solution was prepared by weight, and its volume varied from 1 to 1.5 cc. The weight of the specimens varied around 0.5 gram. The time necessary for establishing equilibrium was about ten days, as was determined by specially arranged kinetic experiments in the apparatus described above. The composition of the rubber mixture was (in parts by weight): natural rubber 100, condensate K-1 1.25, sulfur 4, Aldene 1, zinc oxide 25, lamp black 35, whiting 50, stearic acid 1, and pitch 2. This was cut up into rectangular specimens 2 mm. thick, weighing about 0.5 gram. They were then digested in 30 parts of benzene for three days; the latter was changed every day; then they were digested for two days in benzene to which increasing quantities of anhydrous alcohol had been added, and were then brought to constant weight in a vacuum in darkness. This process resulted in a weight loss of 3 per cent of the rubber.

The specimens were insoluble in the binary mixtures studied, and were kept dry till the end of the experiment, when they swelled in the vapors. This was essential for the increased accuracy of measurement of the degree of swelling, and particularly for the increased accuracy of the subsequent analysis of the

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Kolloidnyi Zhurnal*, Vol. 15, No. 1, pages 60–68 (1953).

specimen and the solution. The effectiveness of the digestion was verified in the following way. The extracted specimens were swelled for ten days in benzene vapor in the apparatus shown in Figure 1, then distilled water was saturated with benzene from the lower bulb of the apparatus and the concentration of the solution thus obtained was measured by an interferometer. The readings of the interferometer to an accuracy of two units on the drum coincided with those for water saturated with the original cryoscopic benzene, while the unwashed rubber caused an increase of the reading of the interferometer of 100 or more units.

After an experiment was finished, the upper part of the apparatus was opened, and the specimen was removed for weighing and washing in a flask with a ground stopper, containing 15 cc. of distilled water, and the equilibrium solution from the lower phase was quantitatively transferred to a graduated 100-cc. flask, and the alcohol concentration in the resulting solution was measured with a Zeiss interferometer. The water with which the swollen specimens were washed was also analyzed.

FIG. 1.—Apparatus for the study of swelling in a vapor.

The calibration graphs of the data of the interferometer were constructed from measurements of alcohol solutions of known concentration in water saturated with benzene. The water extracts of the swollen specimens were saturated with benzene by addition of a drop of benzene directly into the chamber of the interferometer. The possible error in the distribution of alcohol between 5 cc. of solution and the drop of benzene did not exceed 0.1 per cent. Thus, the coefficient of distribution of *n*-butyl alcohol between water and benzene is, according to our measurements, 0.31, and for alcohols, of course, has higher values. Confirmatory experiments showed that the quantitative elimination of the three lower alcohols from the swollen specimen is complete with a single digestion for two days. For the quantitative elimination of *n*-butyl and *n*-hexyl alcohols, double and triple digestion, respectively, are necessary. The possibility of complete elimination of alcohol from rubber specimens was verified by the authors with specimens swollen in pure alcohols. Complete elimination of the liquid in a swollen specimen which had been in water was observed by Mezhenny and Nekryach[5]. In the great majority of cases the amount of alcohol, determined in the system by analysis of the equilibrium solution, agreed with the amount determined by analysis of the specimen. In analyzing a specimen, a small correction for the solution of non-swollen specimen during two days in 15 cc. of water was made. As an illustration of this, Table 1 gives data for the system: *n*-butyl alcohol and benzene.

TABLE 1

CONTENT OF *n*-BUTYL ALCOHOL IN SPECIMENS

N_2 of equilibrium solution	Weight of specimen (g.)	m_2 (mg. alcohol removed by washing of specimen)	m_2' (mg. alcohol in solution)
0.051	0.4485	8.2	10.5
0.055	0.5142	15.0	15.1
0.103	0.4893	25.8	24.5
0.230	0.5013	31.4	29.9
0.374	0.4794	37.7	37.9
0.458	0.4824	31.3	30.8
0.744	0.5034	37.5	34.6
0.950	0.4548	27.0	25.0

In this table, m_2 is the number of milligrams of alcohol in the specimen, removed by digestion, and m_2' is that found by analysis of the solution. The results obtained by both methods are averaged. The deviation from the mean does not exceed 5 per cent in most cases. However, in dilute solutions, deviations reach 10 per cent and higher. By making a large number of experiments on dilute solutions and then graphically averaging the results, we were also able to determine the distribution of the components of dilute solutions with an accuracy of about 5 per cent. In the final calculations, we introduced, by means of graphs of the partial pressures of the vapors of the components, corrections which allowed for the amounts of these in the gaseous phase of the apparatus. These graphs were constructed from data on the activity of benzene in alcohol-benzene solutions obtained by one of the authors[6] and data on the composition of the saturated vapor of these solutions[7].

The swelling of rubber was studied, as well as the distribution of the components between the rubber and the solution in the following systems: methyl alcohol-benzene, ethyl alcohol-benzene, *n*-propyl alcohol-benzene, *n*-butyl alcohol-benzene, and *n*-hexanol-benzene (in purifying the alcohols we utilized the method described earlier[6]). The measurements were made in an air thermostat at 20° ± 1° C. In the octadecanol-benzene system, the degrees of swelling were measured at 60° C in the liquid phase.

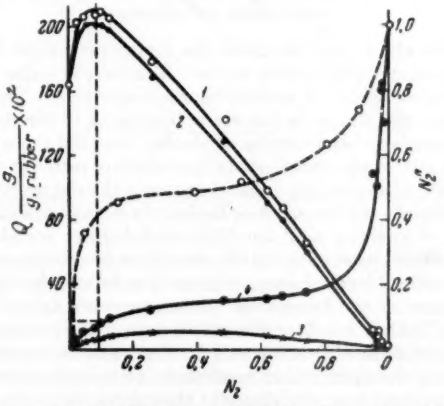


FIG. 2.—Rubber-benzene-methyl alcohol system. 1—Total swelling. 2—Swelling for benzene. 3—Swelling for alcohol. 4—Molar fraction of alcohol in the rubber. The broken line indicates the molar fraction of alcohol in the vapor.

The experimental data obtained are shown in the form of swelling $\left(Q\frac{\text{g.}}{\text{g. rubber}}\times 10^2\right)$-molar fraction of equilibrium solution (N_2) curves and in the form of molar fraction of alcohol in polymer phase (N_2^p)-molar fraction of solution curves. For all the systems enumerated, similar curves were obtained; thus, in Figure 2, the curves are examples of one particular system, the methyl alcohol-benzene system. It is necessary to bear in mind that the lower the molecular weight of the alcohol, the higher the swelling-composition curve on the graph. The same curves for the *n*-hexanol-benzene system deviate somewhat from the curves of the other alcohols, so they are shown separately in Figure 3.

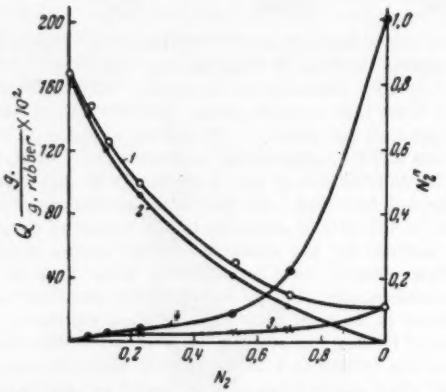


FIG. 3.—Rubber-*n*-hexyl alcohol-benzene system. 1—Total swelling. 2—Swelling for benzene. 3—Swelling for alcohol. 4—Molar fraction for alcohol in rubber.

DISCUSSION OF RESULTS OBTAINED

DEGREE OF SWELLING, COEFFICIENT OF DISTRIBUTION, AND STRUCTURE OF SOLUTIONS

It was shown above that the lower the molecular weight of an alcohol, the higher is the swelling-composition curve. This fact is quite natural from the viewpoint of the structure of alcohol-benzene solutions. The shorter the hydrocarbon chain, the weaker is the steric hindrance to the formation of a hydrogen bond between the molecules of alcohol, and the more effectively is the benzene forced out of the quasi-crystalline solution into the polymer phase.

The existence of a close relationship between the degree of swelling and the structure of solutions is illustrated in Table 2, in which are compared the values of the degree of swelling and the Kirkwood-Anselm correlation parameter, which characterizes quantitatively the structure of solutions[8]. The comparison was made with identical compositions of solutions for the different coalhols. The values of the correlation parameter were taken from work cited above[6]. From Table 2 it is clear that, in all cases, there is a parallelism between the change in the degree of swelling and the change in the correlation parameter.

The values of the distribution coefficients of benzene between both phases decrease, as is evident from the slopes of the curves $N_2^p - N_2$ at $N_2 = 1$, from the value 16.6 in a methyl alcohol-benzene system (see Figure 2) to a value of

TABLE 2

DEGREE OF SWELLING AND KIRKWOOD–ANSELM CORRELATION PARAMETER

Alcohols	N_2	grams	Q	N_2	grams	Q	N_2	grams	Q	N_2	grams	Q	N_2	grams	Q
Methyl	0.3	2.26	171	0.4	2.54	151	0.5	2.82	128	0.6	2.98	104	0.7	3.04	79
Ethyl	0.3	1.90	159	0.4	2.30	139	0.5	2.70	118	0.6	2.97	97	0.7	3.16	72
n-Propyl	0.3	1.85	147	0.4	2.22	127	0.5	2.58	105	0.6	2.85	83	0.7	3.07	60
n-Butyl	0.3	1.83	130	0.4	2.12	111	0.5	2.40	91	0.6	2.69	70	0.7	2.95	52

6.4 in an *n*-hexanol benzene system (Figure 3). In the same way, the "hardness" of structure of pure alcohols decreases. The higher the molecular weight of the alcohol, the less pronounced is its quasicrystalline structure and the higher is the degree of swelling of the polymer in pure alcohol. But the coefficient of distribution of benzene between both phases, and, consequently, the initial slope of the swelling-composition curves decreases with an increase of the molecular weight of the alcohol. From this it follows that in the range of compositions bordering on pure alcohols, the swelling-composition curves must intersect; this was actually observed, as is seen in Figure 4. The value of the coefficient of distribution of benzene between both phases is determined to a large degree by the nature of the polymer. In Figure 2, the broken curve represents the composition of the saturated vapor-composition solution for methyl alcohol-benzene[7] at 20° C. Figure 2 shows that the coefficient of distribution of benzene between the polymer and solution is 3.7 times greater than the coefficient of distribution between the vapor and solution. The selective

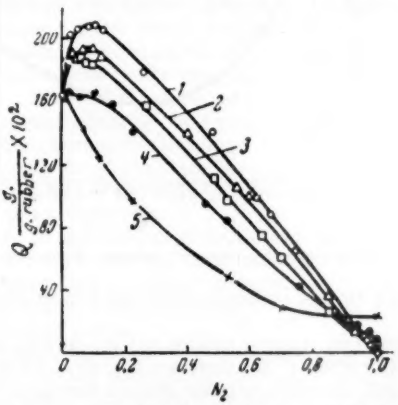


FIG. 4.—Swelling-composition curves. 1—Methyl alcohol-benzene. 2—Ethyl alcohol-benzene. 3—Propyl alcohol—benzene. 4—Butyl alcohol-benzene. 5—Hexyl alcohol-benzene.

absorption of benzene by the polymer leads to an increase of the number of possible configurations between the chain segments and the benzene molecules and, consequently, to an increase of the entropy of the system[9]. With an increase of the length of the hydrocarbon chain of the alcohol, the increase of entropy of the system is observed to an ever increasing degree because of the greater number of configurations between the benzene molecules and the segments of the hydrocarbon chains of the alcohols and to an ever decreasing degree because of the passage of the benzene into the polymer phase.

The coefficient of distribution of alcohol between the polymer and solution decreases, as is seen from the slopes of the curves $N_2^p - N_2$ at $N_2 = 0$, from a value 1.6 in the methyl alcohol-benzene system to a value 0.3 in the *n*-hexyl alcohol-benzene system. In this change of the coefficient of distribution is reflected the dipolar nature of the alcohol molecules, as well as the character of the reaction of these molecules with the chains of the high polymer. In the methyl alcohol molecules, the influence of the polar group is dominant, and they are forced out of the dilute solution into the polymer phase, since this process insures an additional decrease of free energy of the system because of the reaction of the polar group of the alcohol molecules with the rubber. In more concentrated alcohol solutions, the process which involves the greatest loss of free energy in the system is the formation of hydrogen bonds between the alcohol molecules in solution. In fact, Figures 2 and 3 show that, even in the range of extremely dilute solutions, the alcohol concentration in the solution becomes greater than that in the polymer phase. We assume from this that

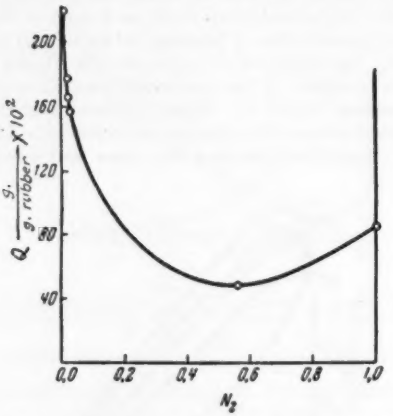


FIG. 5.—System of rubber-octadecanol-benzene. Temperature 60° C.

the reaction of the alcohol molecules with the rubber chains is of a dipole-dipole nature.

In the transition from methyl alcohol to the following alcohols, the role of the nonpolar hydrocarbon chain increases rapidly. Thus in *n*-hexanol, the tendency to pass into the polymer phase sharply decreases; this is evident both in the small value of the coefficient of distribution, and in the form of the swelling-composition curve, which becomes bent towards the abscissa. In the passage to alcohols of greater molecular weight, the increase of this tendency can lead to a minimum on the swelling composition curve; this was also observed in the *n*-octadecanol-benzene system at 60° C, as is seen in Figure 5.

The curves of the molar fraction of alcohol in N_2^p polymer phase-molar fraction of alcohol in solution (N_2) closely resembles the saturated vapor-solution composition curves[7]. This is seen in Figure 2, in which both curves are depicted. The appearance of a flat section in the curves of distribution between the polymer and solution phases attests to the fact that the polymer, as in the vapor phase, absorbs only single alcohol molecules; otherwise it is

difficult to understand why, with an increase of alcohol concentration in solution, the concentration in the polymer phase increases extremely slowly. In Figure 2 we see that, in the whole range of change of composition, the molar fraction of the alcohol in the vapor phase is greater than the molar fraction in the polymer phase, and in the middle range of concentrations the ratio of these molar fractions is equal to approximately 3. The fact that the volatility of alcohol in the polymer phase becomes equal to its volatility in the vapor phase with a much smaller alcohol concentration, can be explained only by assuming that the alcohol in the polymer is in the form of isolated molecules, which are energetically drawn out of this phase. Gee's assumption of the possibility of absorption by the polymer of the associated molecules of the alcohol[10] is not confirmed by our experiments.

THE NATURE OF THE EXTREMES ON THE SWELLING–COMPOSITION CURVES

In systems in which lower alcohols are present, a maximum is observed on the swelling-composition curve, which is most pronounced for the methyl alcohol-benzene-system and has a value at the molar fraction of alcohol of 0.09. In systems with ethyl and *n*-propyl alcohols, the values of the maximum are smaller and their positions are displaced to the region of smaller alcohol concentrations. In the systems noted, the coefficients of distribution of both components are greater than unity; that is, for the polymer phase in equilibrium with dilute alcohol solutions with alcohol added and in equilibrium with dilute benzene-benzene solutions. From this it follows that a point exists on the curve of isothermic equilibrium, at which the composition of the binary solution in the polymer phase is the same as the composition in the solution phase. At this point a maximum is observed on the swelling-composition curve, as is distinctly seen from a comparison of the swelling and distribution curves in Figure 2. In systems containing normal butyl and *n*-hexyl alcohols, the coefficients of distribution of the alcohols are less than unity, while the coefficients of distribution of benzene are greater than unity, and the maxima on the swelling-composition curves disappear.

This reasoning leads to the conclusion that the minimum on the swelling-composition curve will be observed in those cases where the coefficients of distribution of both components are less than unity.

An example of this, as is seen in the swelling-composition curve in Figure 5, is the *n*-octadecanol-benzene system.

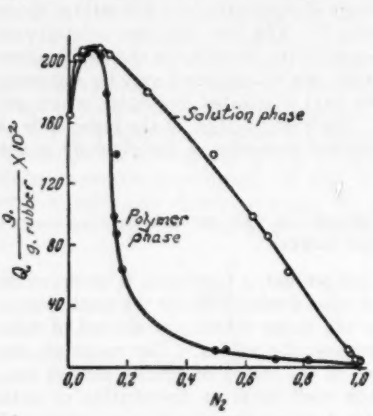
From this generalization it follows that the distribution of the components of a binary mixture between the polymer and solution phases is in accord with the hypothesis of Konovalov[4]. At the extreme point on the swelling-curve, the composition of both phases is the same, and, conversely, the equivalence of composition of both phases is a necessary condition of the appearance of an extreme on the swelling curve. The degree of swelling increases with an increase of concentration of the component which is present in highest concentration in the polymer.

In Figures 6 and 7 we see that, during swelling of a polymer, a greater change of concentration is observed than during evaporation; consequently, the swelling of a polymer can serve as a means of distinguishing mixtures of polar substances and non-polar substances.

From the point of view of thermodynamics, the necessity of the appearance of maxima on the swelling curves follows from a study of the curves of partial

free energies of the components, calculated by means of the data concerning activity in binary solutions (U).

As an illustration of this, Figures 8 and 9 show the curves of partial free energy of ethyl and n-butyl alcohols in the polymer and solution phases.



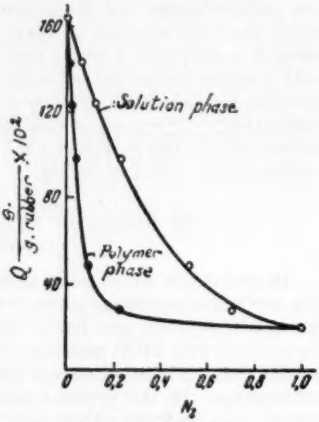


FIG. 6.—Example of the application of the first and second laws of Konovalov to the swelling of a polymer in rubber-methyl alcohol-benzene.
FIG. 7.—Example of the application of the second law of Konovalov to the swelling of a polymer in rubber-n-hexyl alcohol-benzene.

In Figures 8 and 9, it is seen that, when $N_2 = 0.065$, the curve of partial free energy of ethyl alcohol in the polymer phase intersects the curve for the solution phase, and in the range of more dilute solutions passes beneath it. Thus, starting from the molar fraction of alcohol 0.065 and below, the passage of alcohol into the polymer phase is accompanied by a great decrease of free energy in comparison to its passage into the solution phase. The additional

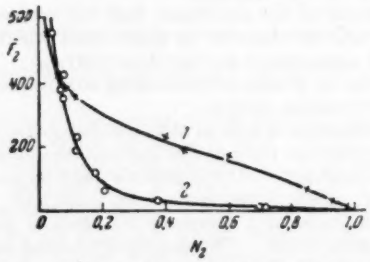


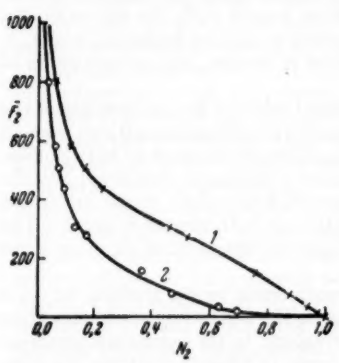
FIG. 8.—Partial free energy of ethyl alcohol. 1—Solution phase. 2—Polymer phase.

absorption of alcohol, starting from this concentration, causes a sharp increase of the potential barrier of the chains of the polymer and a decrease of their flexibility, which causes a decrease of the amount of benzene absorbed. This explains the fact that, in systems showing a maximum on the swelling curves, the partial absorption of benzene also passes through a maximum, as is seen in Figure 2. In other words, the excess accumulation of alcohol shifts its chemical

potential in the polymer phase with the range of more concentrated solutions, and the necessity of equalizing the chemical potentials of benzene in both phases requires an additional absorption of benzene by the polymer phase. To the right of the maximum point, the reverse phenomenon is observed.

From Figure 9 it is clear that in a rubber-*n*-butyl alcohol-benzene system, which does not show a maximum on the swelling curve, the curves of partial free energy of the alcohol in the solution and in the polymer phase do not intersect anywhere.

In accord with the aim of the investigation, it seemed desirable to prove by an independent method the existence on the swelling curves of points of constant composition. The volumetric study of swelling proposed by one of the authors was selected as the method. The essential feature is the measurement of the volume in a metallic condenser of the Nernst type, with a movable plate which can be shifted in a vertical direction by means of a micrometric device. Six cc. of solution were placed in the condenser and the specimen to be swollen



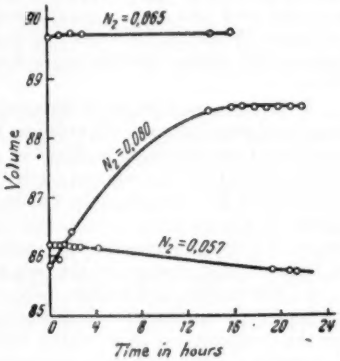


FIG. 9.—Potential free energy of *n*-butyl alcohol. 1—Solution phase. 2—Polymer phase.
FIG. 10.—Curves of the readings of the condenser (in degrees).

was suspended in the vapor phase, between the electrodes of the condenser. Swelling was studied by following the change of volume with time. Figure 10 shows the results obtained with a polymer-ethyl alcohol-benzene system for three different solutions: azeotropic ($N_2 = 0.065$), one lying to the left of the azeotropic point ($N_2 = 0.057$) and one lying to the right of it ($N_2 = 0.080$).

From Figure 10 it is clear that, when $N_2 = 0.065$, the volume in the condenser for 15 hours does not change with time; that is, the polymer absorbs the solution of composition $N_2 = 0.065$. Furthermore, we see that, from a solution of molar part, $N_2 = 0.057$, the polymer absorbs primarily the alcohol and the volume decreases; finally, from a solution of molar part, $N_2 = 0.080$, benzene is primarily absorbed and the volume increases.

CONCLUSIONS

1. The swelling in the gaseous phase at 20° C of a digested vulcanizate of natural rubber was studied through the entire range of compositions of the following binary systems: methyl alcohol-benzene, ethyl alcohol-benzene, *n*-propyl alcohol-benzene, *n*-butyl alcohol-benzene, and *n*-hexanol-benzene,

and in a system of octadecanol-benzene at 60° V in the liquid phase. The swelling-composition curves show a maximum in the first three systems enumerated and a minimum in the latter system.

2. In the first five systems, the concentrations of the components of the equilibrium solution phase and the rubber phase were measured by means of an interferometer.

3. The coefficient of distribution of alcohol between the polymer and solution phases decreased from 1.6 in the methyl alcohol-benzene system to 0.3 in the *n*-hexanol-benzene system. The decrease of the coefficient of distribution of alcohol through the series of homologs is attributable to the dipolar character of the alcohol molecules. The coefficient of distribution of benzene between the two phases decreased from 16.6 in the methyl alcohol-benzene system to 6.3 in the *n*-hexanol-benzene system. This decrease of the coefficient of distribution of benzene is caused by the weakening of the quasi-crystalline structure in passing from methyl alcohol to the higher alcohols.

4. From an analysis of the distribution of alcohol between the solution and polymer, and also from a comparison of these curves with the curves of distribution of alcohol between the binary solution and its saturated vapor, it follows that rubber absorbs individual alcohol molecules, but not associates of them.

5. From a comparison of data on the distribution of the components of the binary solution between the polymer and equilibrium solution, and also from an analysis of the curves of partial free energy of the components of both phases, it follows that the general nature of the curves of isothermic equilibrium in the systems studied accords with the hypothesis of Konovalov; at the maximum points on the swelling curves, the composition of both phases is equal. The degree of swelling increases with increase of the concentration of the component in highest concentration in the polymer.

6. The existence of points of constant composition on the swelling curves is confirmed by measurements of the swelling by the volumetric method. Only for the compositions of solutions which correspond to the maximum points on the swelling curves, the volume in the condenser in whose vapors the specimen is suspended does not change with time. In more dilute solutions, the volume decreases; in more concentrated solutions it increases, with time.

7. There is a close relation between the degree of swelling and the structure of a solution. The more pronounced the quasi-crystalline structure of the solution, the higher is the swelling-composition curve on the graph. The values of the degree of swelling and the Kirkwood-Anselm correlation parameter change in parallel for a given composition of the solution, in passing from one alcohol to another.

REFERENCES

[1] Gee, *Trans. Faraday Soc.* **40**, 463 (1944); Magat, *J. Chem. Phys.* **46**, 352 (1949).
[2] Dubry, *J. Chem. Phys.* **36**, 387 (1938); Smolitza and Kalbanovskaya, *Kolloid. Zh.* **10**, 369 (1948); Vilenski and Matveyeva, *Kolloid. Zh.* **13**, 412 (1951).
[3] Bronsted and Volgvartz, *Trans. Faraday Soc.* **36**, 619 (1940); Gee, *Trans. Faraday Soc.* **40**, 478 (1944); Breitenbach and Frank, *Monats.* **67**, 282 (1946).
[4] Konovalov, "Elasticity of vapor of solutions", St. Petersburg, **1884**, p. 37.
[5] Mezhenny and Nekryach, *Ukr. Chem. J.* **14**, 133 (1948).
[6] Starobinets, Starobinets, and Ryzhikova, *J. Phys. Chem.* **25**, 1186 (1951).
[7] Tryhorn and Wyatt, *Trans. Faraday Soc.* **24**, 40 (1928).
[8] Skanari, "Physics of dielectries", Goschimizdat Tech.-Teor. Lit., **1949**, p. 108.
[9] Tager, "Solutions of high molecular compounds", Goschimizdat (Gov. Chem. Pub.), **1951**, p. 115.
[10] Gee, "Chemistry of large molecules", Goschimizdat Coll. 1, **1948**, p. 190.

OZONE CRACKING
A CINEMATOGRAPHIC STUDY *

DOREEN M. SMITH AND V. E. GOUGH

DUNLOP RESEARCH CENTRE, DUNLOP RUBBER CO., LTD., FORT DUNLOP, ERDINGTON, BIRMINGHAM, ENGLAND

INTRODUCTION

Powell and Gough[1] have suggested that two things must be considered when estimating ozone cracking: first, the probability of a crack forming under the given conditions of stress, exposure, and concentration and, second, the rate at which cracks grow when formed. They also argued that growth depends on a stress concentration existing at the end of a crack. A study of the formation and growth of cracks will inevitably lead to a better understanding of the nature of the laws governing the process.

Cine films have long been used in the study of growth of leaves and flowers of plants, and the technique of time-lapse photography has been developed for this specific purpose. The film so produced shows the complete growth process in a period of time occupying a fraction of the actual. From this followed the idea that the development of cracks could profitably be studied by time-lapse cine-micrography. In addition to giving the full cracking process as a fairly rapidly changing picture, covering the whole test in a few minutes, and enabling an overall idea of the process in time to be gleaned, the film allows an observer to follow the progress of an individual crack from its inception. The film is particularly useful in enabling a profitable number of stills to be selected for detailed study and measurement.

APPARATUS

The apparatus consists of a cine-camera and driving motor, a microscope, a light source, and a rubber specimen stretched in an ozone chamber (see Figure 1).

The specimen is held stretched behind a glass window in the ozone chamber. The specimen support is made of aluminum (since this is a poor catalyst to ozone decomposition) and the ends of the specimen are clamped between aluminum strips 13 cm. apart. The area photographed (approximately 12 sq. mm.) is at the center of a long specimen, and it is reasonable to assume that the area is under uniform strain and is not affected by irregularities in clamping pressure. In order to minimize localized cracking around scratches and surface irregularities on the rubber, all samples are molded against a polished stainless-steel plate with a mirror finish or against a smooth plate of glass. Since light accelerates ozone decomposition, the illumination is weak, and the glass window through which it is directed is small.

A 16 mm. cine-camera (Kodak 25 mm. lens) is geared to a synchronous motor. With half-open shutter (90° open and 270° closed), one three-second

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 5, pages 219–237, October 1953.

exposure is taken every 12 seconds. Projection of the completed film is 192 times as fast. The microscope magnification can be varied slight by extension of the objective-eyepiece distance; this varies the area photographed from 6–12 sq. mm.

FILM ANALYSIS

Since the films described here were taken to establish the procedure and to show the potential value of the technique, no special effort was taken to stabilize conditions. The concentration of ozone under which the rubber was filmed was different in each case, the microscope magnification differed, and each sample came from separately mixed batches and from slabs molded at different times. For these reasons, comparisons of these films must be made with some reservations. But a discussion of the features of each film will indicate the nature of the laws governing ozone cracking.

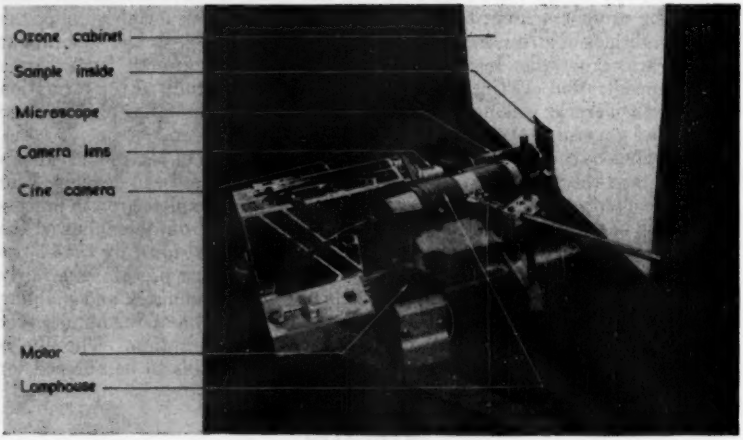


FIG. 1.—Apparatus.

The variation of number of cracks with time, the rate of growth of individual crack lengths, and the distribution of cracks over the surface area were studied in each case. To determine the variation of the number of cracks with time, a tracing of the image of the cracks given by an episcope or film viewer was made from every tenth or twentieth frame. In the early stages of crack initiation, crack images were neither easily nor certainly recognized. For this reason, cracks were counted as appearing for the first time in any particular frame only provided they were identified without doubt in the next frame examined. By comparing tracing sheets of early stages with those of later stages and vice-versa, crack joining and disappearance were identified. The counts were continued until the rate of increase was one crack or less in 10 frames or two minutes' exposure to ozone. This involved a considerable amount of labor, especially since two people made the counts independently and any case of a difference greater than one crack was investigated so as to eliminate errors due to mistakes in identification and copying. Rates of growth of individual crack lengths were determined by identifying and tracing particular cracks carefully.

The distribution of cracks over the surface area was studied by dividing the frame image into squares of equal area and counting the number of crack centers per square.

RESULTS

The cracks form generally over the whole surface in a manner somewhat similar to the distribution of raindrops on a pool of water which would be recorded on an instantaneous photograph. Analysis shows no significant departure from a Poissonian distribution.

Visible cracks do not form instantaneously, but require a delay period. Nor do the cracks form simultaneously. Analysis suggests that rate of crack formation is statistically distributed in time. Even during the formation period, some cracks disappear and others join.

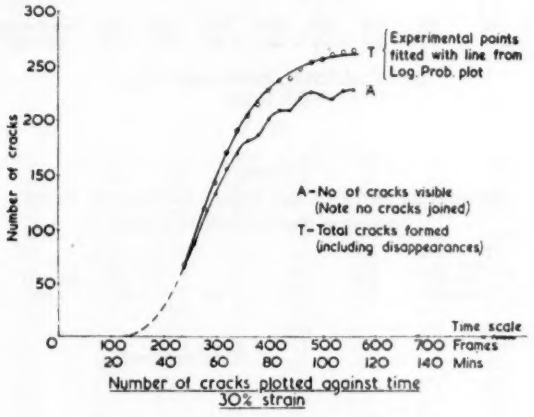


FIG. 2.

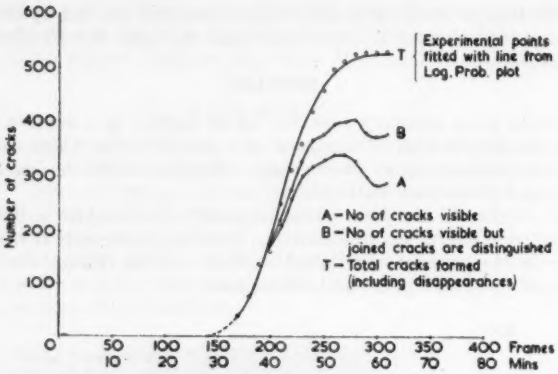
There are no identifiable distinguishing marks on the surface at the points where cracks form, provided there are no surface imperfections due to scratches on the mold face. Reverse running of the film confirms this.

After the formation period, the cracking continues to develop as long as both stress and ozone are present although no more new cracks appear. During this development there are disappearances and, also, crack joining continues. In some cases, therefore, the number of visible cracks markedly decreases.

The results of the film analysis are now dealt with in detail.

THE VARIATION OF THE NUMBER OF CRACKS WITH TIME

The number of cracks was plotted against time on ordinary graph paper (Figures 2 and 3 from Tables 1 and 2). There are three plots namely A, B and T in Figure 3. A is the number of visible cracks; B is the number of visible cracks, but joined cracks are distinguished (that is they are counted as separate cracks); T is the total number of cracks formed (including disappearances). Curves A and T only are shown in Figure 2, since curve B coincides with A, there being no joining of cracks. Examination of the plot T (total crack num-



Number of cracks plotted against time
15% strain

FIG. 3.

TABLE 1

RUBBER AT 30 PER CENT STRAIN EXPOSED TO OZONE

Number of cracks at different times

Frame number	Time from first exposure in minutes	(1) and (2)	(3)	(4)	A or B (1)+(3) or (2)+(3)	T (2)+(3)+(4)	Per cent T 100% =264
0 50 100 150 200			None observed				
238	47.6	67	—	—	67	67	25.4
258	51.6	87	—	2	87	89	33.7
278	55.6	116	—	2	116	118	44.7
298	59.6	132	—	10	132	142	53.8
318	63.6	153	—	16	153	169	64.0
338	67.6	167	1	20	168	188	71.2
358	71.6	177	3	23	180	203	76.9
378	75.6	179	6	28	185	213	80.7
398	79.6	191	9	28	200	227	86.0
418	83.6	194	15	28	209	236	89.4
438	87.6	189	18	31	207	238	90.2
458	91.6	196	24	27	220	247	93.6
478	95.6	197	28	27	225	252	95.5
498	99.6	193	29	33	222	255	96.6
518	103.6	195	24	40	219	259	98.1
538	107.6	194	33	34	227	261	98.9
558	111.6	193	34	36	227	263	99.6

(1) Joined cracks counted as one. Reappearances ignored. Disappearances not counted.
(2) Joined cracks distinguished. Reappearances ignored. Disappearances not counted.
(3) Reappearances.
(4) Disappearances.

A {Joined cracks counted as one.
(1)+(3) {Reappearances counted. Disappearances ignored.
B {Joined cracks distinguished.
(2)+(3) {Reappearances counted. Disappearances ignored.
T {Joined cracks distinguished.
(2)+(3)+(4) {Reappearances and Disappearances counted.

ber) against time indicates that the function may be a probit. This is the curve which arises when the rate of crack formation is normally distributed in time. The values of T at any time were converted to a percentage of the total number of cracks recorded and a plot was made on arithmetical probability paper. This gave a reasonably straight line, and the corresponding probit was drawn.

A normal distribution on linear time demands the possibility of cracks arising at negative times, that is, before exposure to ozone. This is absurd and is overcome by replacing time by its logarithm. The probit curve derived from

TABLE 2

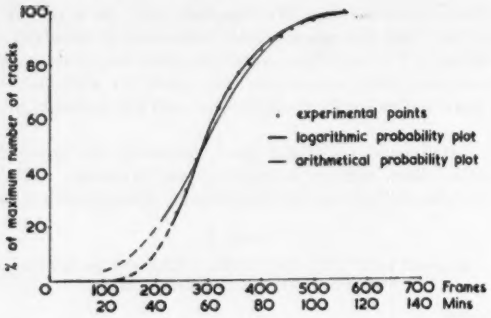
RUBBER AT 15 PER CENT STRAIN EXPOSED TO OZONE
Numbers of cracks at different times.

Frame number	Time from first exposure in minutes	(1)	(2)	(3)	(4)	A (1)+(3)	B (2)+(3)	T (2)+(3)+(4)	Per cent T 100% =527
0	0	None observed							
50	10								
100	20								
150	30								
170	34	39	39	0	0	39	39	39	7.4
180	36	69	69	0	3	69	69	72	13.7
190	38	130	130	0	4	130	130	134	25.4
200	40	171	171	0	8	171	171	179	34.0
210	42	208	215	2	27	210	217	244	46.3
220	44	254	269	2	36	256	271	307	58.3
230	46	289	314	9	36	298	323	359	68.1
240	48	317	356	8	54	315	364	418	79.5
250	50	315	366	8	83	323	374	457	86.5
260	52	323	377	15	104	338	392	496	94.2
270	54	315	377	22	111	337	399	510	97.0
280	56	294	370	30	121	324	400	521	99.0
290	58	254	336	41	148	295	377	525	99.5
300	60	247	337	33	155	280	370	525	99.5
310	62	241	331	41	155	282	372	527	100
400	80					282			
500	100					238			
1000	200					158			
1500	300					117			
2000	400					96			
2500	500					79			
3000	600					63			
3500	700					49			

Notation as Table 1.

a plot on logarithmic probability paper fits the data better than the probit on a linear time basis (Figure 4).

A secondary error in determining the probit to fit the points may arise because cracks may still be forming at the time at which the count was taken to be 100 per cent. Theoretically the 100 per cent value is never reached but is approached asymptotically, and the process of continuing to count the cracks per frame for higher time values will not enable us to determine the 100 per cent value unless the counting is continued for an infinite time. A practical solution was found to be to continue to count the cracks in every tenth or twentieth frame until the number of cracks did not change by more than one crack. Then probits calculated for asymptotic values equal and adjacent to the maximum number of cracks observed were plotted on probability paper.

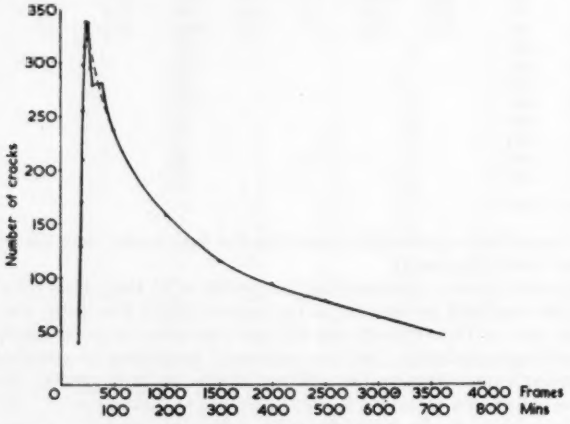


The logarithmic and arithmetical probits plotted on linear scales
30% strain

FIG. 4.

The asymptotic value which gave the minimum residual departure of the points from a straight line was chosen as the correct asymptote. It was adequate to use mean deviations in selecting the asymptote with the minimum residual. In any case, the adjustment to the totals was less than 1 per cent. In this way all counts are used in determining the probit and the best allover fit is obtained for the experimental values in Tables I and II. The number of cracks visible in the frame, *i.e.*, count A, is plotted against time in Figure 5.

The rising curve in the first 50 or 60 minutes is the formation period, already considered in detail in Figure 3. At the closing stages of the formation period



Visible number (A value) plot
15% strain

FIG. 5.

the number of cracks starts to decrease and continues to do so during crack development. The rapidly falling curve of Figure 5 approximates to either of two equations:

$$N = e^{a-t/b} \tag{1}$$

$$N = c - d.\log_e t \tag{2}$$

which are not equivalent. In the present data:

$a = 1$
$b = 435$
$c = 688$
$d = 98$

Equation 1 is the more reasonable because it indicates that the number of cracks falls to zero at infinite time only, while Equation 2 states that there will be no cracks at 1100 minutes and a negative number afterwards.

The 7.5 per cent film could not be analyzed in this way because too few cracks develop in the sample area which is photographed.

THE DISTRIBUTION OF CRACKS OVER THE SURFACE

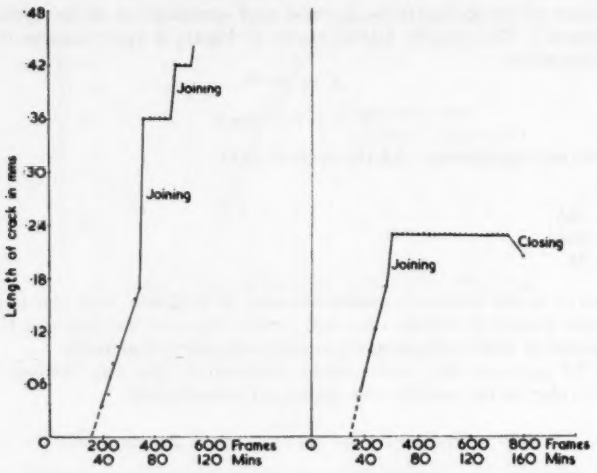
If cracks are both individually and collectively at random, then it can be shown that their distribution should not differ significantly from a Poisson distribution[2]. To test the closeness of the observed crack distribution to a Poisson distribution, a comparison was made of the sample's mean and variance. The ratio of the variance of the number of cracks in a number of equal area regions of the same frame to the mean number of cracks in a region was calculated, and will be called z. Since the probability distribution of z is approximated by a χ^2 distribution with $(N-1)$ degrees of freedom, where N = total number of regions of equal area, we can determine the probability that the z value would arise from chance if the cracks are individually and collectively at random. These statistical checks were carried out on every twentieth frame in the 30 per cent film. In some 20 cases, one instance of a value of $P = 0.005$ occurred, and all the remaining 19 lay between $P = 0.15$ and 0.75. The data, then, did not show significant departure from the Poisson distribution. This shows that the cracks were random at all times during the formation period.

In the case of the 15 per cent film, the sample had been molded against stainless steel instead of glass, and mold scratches had caused some alignment of the cracks. It was not considered worthwhile to carry out a detailed statistical analysis of randomness in this case, since it would be a measure of the randomness of the scratches rather than the nature of the cracking itself.

It was not possible to analyze the 7.5 per cent film for randomness of cracks, since too few cracks were formed. A lower magnification would be necessary to increase the sample area and the number of cracks.

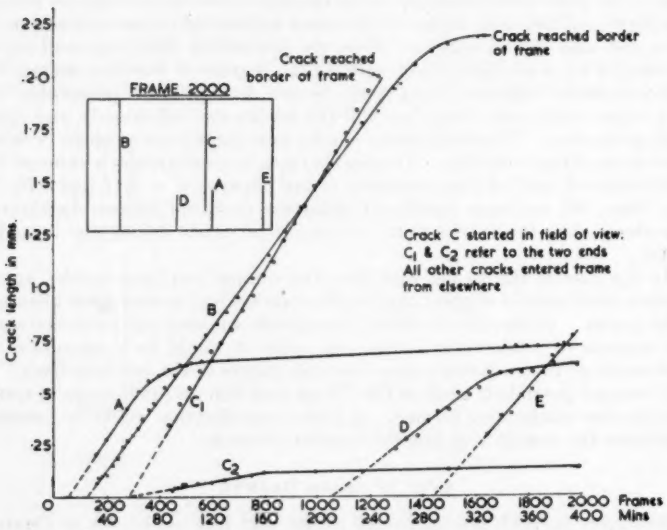
RATE OF CRACK GROWTH

Examples of crack growth in the 15 per cent film are shown in Figure 6. The rate of length growth was found to be constant until two cracks joined or until the crack began to close due to the presence of a larger crack adjacent to it. After crack joining the growth was found to stop. This will be discussed again later.



Examples of crack growth - 15% strain

FIG. 6.



Crack growth
7·5% strain

FIG. 7.

All the cracks of the 7.5 per cent film are recorded on Figure 7. The graphs in this figure are plots of the distance from the starting point (or if the crack started off the screen, of the distance from the screen edge) to the visible end of the crack. Their slopes, therefore, are the rates of growth in one direction. In the case of crack C, the growth in both directions could be plotted. C_1 shows the growth which occurs when there is no overlapping. By overlapping is meant that one end of each crack cuts a line which lies in the direction of the applied stress and which is of course perpendicular to the two cracks. C_2 is the growth of crack C in the opposite direction and will be referred to later.

There are two stages to crack growth. In the first stage there is a steady linear growth in time and, in the second stage, growth is zero. For all cracks, except C_2, the slopes of the graphs in the first stage are substantially the same. Study of the location of the ends of cracks and of the growth curves for the same cracks shows that the changes from steady growth to no growth is due to interaction between adjacent cracks. The decrease in growth rate of crack B

TABLE 3

A SUMMARY OF GROWTH RESULTS

Rubber at 7.5 per cent strain exposed to ozone

Crack	Induction time in minutes	Growth rate on projected picture cm./frame	Growth rate in sample in mm./hour	Frame at which growth rate decreases
A	10	0.015	0.540	340
B	24	0.013	0.490	1390
C	56	0.016	0.600	—
C	56	0.002	0.068	800
D	210	0.008	0.280	1660
E	288	0.003	0.420	2020

NOTE TO TABLES 1, 2 and 3

Direct comparisons between these three tables of number of cracks and times of appearance should not be made because

(1) they represent differently compounded samples.
(2) the samples were not under the same ozone concentration.
(3) the magnification of the microscope and the area of the sample photographed is not the same.
(4) the tests were not carried out on the same occasion.

can be correlated with the overlapping of crack D at frame 1390. Only crack B is affected and D continues to grow at its original rate until frame 1660. The growth rate for crack A begins to decrease (at frame 340) when crack C starts. The growth of C towards A is given by the C_2 plot and the growth rate of C_2 is low. The growth of C away from A is given by C_1 which exhibits a normal growth rate.

We have, then, the following phenomena:

(1) When C (which is $(C_1 + C_2)$) starts, it slows down and ultimately stops the growth of A.
(2) C_2, which tries to grow towards A, grows very slowly and eventually its growth ceases entirely.
(3) C_1 grows away from A and its growth rate is normal.

These results exhibit the importance of stress to crack growth[1], which will be discussed later.

A summary of the growth results for the 7.5 per cent film is given in Table 3.

Typical frames from the three films are shown in Figures 8 to 11.

DISCUSSION OF CRACKING THEORIES IN THE LIGHT OF THE PRESENT RESULTS

The film and preceding results confirm that there are two main phases in the physical development of visible cracks:

(1) the formation of cracks;
(2) the growth of cracks.

The formation of cracks appears to be governed by statistical considerations. The rate of crack formation is log. normally distributed in time, and cracks are randomly distributed over the surface. The growth of cracks, when formed, appears to be linear with time until interference between neighboring cracks or joining of cracks modifies it.

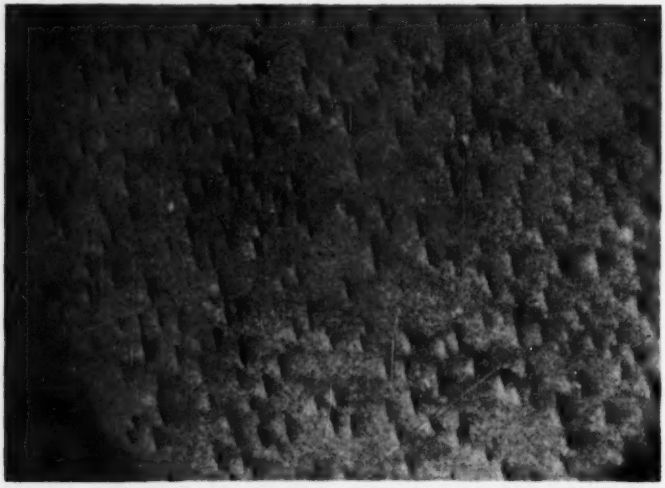


FIG. 8.—Frame number 520 (time of exposure to ozone, 104 minutes) from the film showing the cracking of rubber at 30 per cent strain.

The nature of the interference between neighboring cracks, which is due to stress release, has been already discussed by Newton[3] and by Powell and Gough[1]. The latter base their discussion on St. Venant's principle.

It is generally accepted in the literature that ozone attack (or ozone-catalyzed attack) takes place at the double bonds in the rubber molecule[4]. It is clear, however, that all the double bonds in the surface do not contribute to the formation of a visible crack and even less become the nuclei of visible cracks. There are about 10^{14} or 10^{15} double bonds available in each square centimeter of surface[5]. The number of visible cracks may range from zero to 10^5 to 10^6 per sq. cm., and, in the kind of cracking which has any serious practical consequence, the crack density is not more than 10^2 per sq. cm.

The amount of ozone normally available and the rate of collision with the surface are of the right order for the attack of all surface bonds in a matter of one or two minutes[5]. This is far less than the time to produce the first visible cracks. Therefore it is impossible to attribute crack formation to the existence

FIG. 9.—Frame number 260 (time of exposure to ozone, 52 minutes) from the film showing the cracking of rubber at 15 per cent strain.

of a restricted number of areas where a sufficient number of ozone molecules have reacted, implying that the uncracked regions have been starved of ozone. Also, since more cracks form at high stresses, we are bound to assume that stress plays a part in the formation of a crack. (The results in this paper confirm that stress also plays an important part in crack growth.) It is improbable

FIG. 10.—Frame number 2,640 (time of exposure to ozone, 528 minutes) from the film showing the cracking of rubber at 15 per cent strain. Comparison with photograph 2 shows the considerable reduction in the apparent number of cracks.

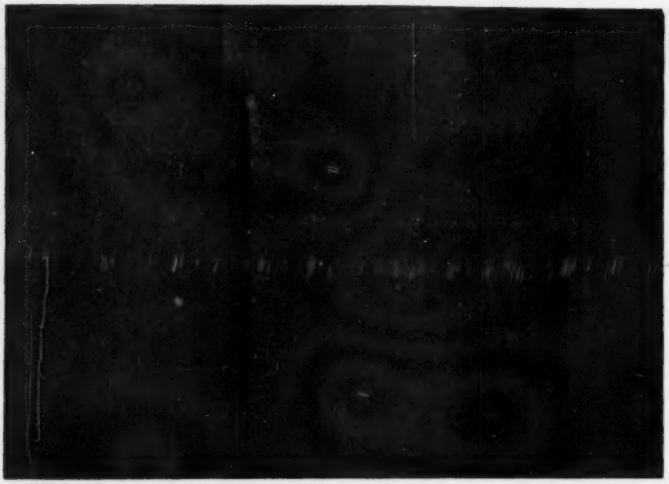


FIG. 11.—Frame number 2000 (time of exposure to ozone, 400 minutes) from the film showing the cracking of rubber at 7.5 per cent strain. This corresponds to the inset of Fig. 7.

that the low stresses arising in cracking test-samples could modify the bond reactivity. For instance, the vibrational frequency of the double bond (measured by infrared absorption) is not measurably altered by strains of less than 400 per cent[6]. Consequently a different mechanism must be proposed to explain:

(1) The discrepancy between the number of double bonds and the number of crack nuclei.
(2) The part played by stress in crack formation.

Because of the results presented in this paper, we propose a possible mechanism of crack formation which is statistical in character (see below).

SUMMARY OF EARLIER THEORIES

The ensuing discussion will be restricted to two theories:

(1) The skin or surface layer theory[7].
(2) Newton's Theory[8].

The skin or surface layer theory postulates:

(1) A statistical variation (on a macroscopic scale) of the physical properties and (or) of the stress over the sample surface.
(2) The formation of a skin or surface layer of different physical properties due to the action of ozone on the rubber either stressed or unstressed. Essentially this skin is weak in tensile strength.

Cracks originate where the surface stress exceeds the tensile strength. The number of such points is limited because of the statistical distributions mentioned. A higher applied stress results in an increase in the number of such points.

Newton's Theory postulates:

(1) The energies of the molecules in the surface are statistically distributed.
(2) Ozone attack at a double bond results in a two-stage process. In the first stage, chemical fission occurs. In the second stage, if stress is absent recombination occurs, but if the stress is above a certain threshold value, recombination is prevented.

It is well known that exposure of an unstressed sample to ozone, followed by stressing (not in ozone), does not produce visible cracks. This would seem to reject the skin or surface layer theory. Exposure to ozone in an unstressed condition does not protect rubber against visible cracking when it is exposed subsequently to ozone in a stressed condition.

Under either of these theories it is difficult to explain the observed distribution of rate of crack formation in time. It may be thought that the effect is due to ozone attack being distributed in time. This is an improbable explanation. The delay between the first visible crack and the last few cracks is about 20 minutes (in the case of the film at 15 per cent strain), which is incompatible with the relatively uniform growth in the initial stage of a crack's development (see Figure 6).

A STATISTICAL THEORY OF CRACK INCEPTION

The theory of ozone cracking can be conveniently divided into three sections:—

(*a*) The mechanism of ozone attack.
(*b*) The mechanism of crack formation.
(*c*) The mechanism of crack growth and development.

The present theory is concerned only with Section (*b*), that is, with the factors settling the number and distribution of the nuclei of visible cracks. Crack growth (Section (*c*)) will be dealt with later. Neither section is intended to include the equation of the chemical reaction at the double bond, or to deal in any way with the chemistry of ozone attack (Section (*a*)). It is assumed, however, that ozone attack at a double bond causes scission and that recombination to the original state normally occurs, but a crack forms when it is prevented.

The following theory arises from the fact that the rate of crack formation is normally distributed in logarithm of time (Figure 4) and the fact that the number of cracks is relatively small, since only one crack arises in an area containing between 10^9 and 10^{15} double bonds. Of necessity, the theory starts with a postulate, but its justification lies in the deductions from it, which agree with observations.

Consider any small region on or near the rubber surface. Segments of a number of molecules pass through it at any instant. Assuming a random orientation, approximately one-third of these molecules will, by average, be primarily responsible for carrying the applied uniaxial tension. There will be statistical fluctuations from the average of one-third. At any given instant there will be a small proportion of regions which have a preponderance of segments of molecules primarily responsible for carrying applied uniaxial tension. Consider such a region.

A crack arises at that region only if several double bonds, one in each of the segments in the several molecules, are simultaneously attacked by ozone. The

simultaneous breaking by ozone of adjacent stress-carrying molecules (or segments thereof) at the points where these molecules pass through a plane perpendicular to the applied stress results in the movement apart of the free radicals or molecule ends by an amount sufficient to constitute a permanent physical or mechanical discontinuity, and recombination of the free radicals or molecule ends is prevented.

The number of bonds involved must be such that the distance of separation of the central radicals is sufficient for recombination to be prevented and enough stress exists at the crack's extremities for the crack to grow.

It is possible, therefore, to postulate that the number of bonds involved in the start of a crack is greatest at low stresses and smallest at high stresses, fewer bond breaks being required at a high stress to obtain the same distance of separation of the central radicals. If an isolated double bond is in a segment of a molecule primarily concerned with carrying the applied stress, its "more rigid" neighbors which have no attacked bonds support the stress and prevent sufficient movement apart of the radicals to cause a permanent break. Once the break of the several adjacent bonds is initiated, there is a sufficient increase in stress intensity at those segments of the molecules located at the ends of the newly-formed crack for growth to be ensured, for even a single double bond in this very highly stressed region will fail when attacked by ozone. In this way the rubber which experiences an increase in stress can now become cracked, and crack growth can take place through rubber which may otherwise have been unaffected.

The idea is somewhat akin to the importance of the randomness in location of the ends of individual fibers in a sliver of wool or cotton in maintaining the full strength. When a fair number have their ends adjacent, a local weakness arises. The comparison breaks down, however, when pursued further. Owing to the kinetic nature of the rubber molecules, the sliver of wool is best replaced by a tube full of eels.

Since the molecules in the rubber are continually in motion, the description of their location and condition has to be stated in statistical terms and must involve the idea of probability. The probability of a crack being initiated at a given time can be expressed in terms of the continued product of several probabilities raised to the power n, where n is the number of molecules involved.

Consider a very small area of the surface of such a size that, on the average, one double bond would be expected to appear on it. The probability of a bond, situated in a segment of a molecule primarily responsible for carrying the applied stress (probably lying in a direction approximating to that of the applied stress) being attacked by ozone is the continued product of several probabilities. These are the probability of the segment of the molecule being in the appropriate direction, the probability of a double bond being in the chosen region, the probability of an ozone molecule being available, and the probability of the reaction with the double bond occurring. Some, at least of these probabilities are small and their product is inevitably smaller, since none can be greater than unity.

The probability of n adjacent molecules being attacked under similar conditions at the same time would be given by this continued product being raised to the power n, since the molecules are substantially independent.

A proper analysis would be more elaborate and would require the simple probabilities to be replaced by distribution curves which would be functions of location and time.

It may be argued that there are no particular molecules which are primarily responsible for carrying an applied uniaxial tension and that all molecules contribute equally. However, the application of a stress in a particular direction must affect some molecules differently from others; otherwise the material would act like a gas and would require a uniform external pressure. It is when several of these particular molecules, which happen to be neighbors are simultaneously attacked by ozone that a crack is initiated.

These modifications in no way alter the essence of the argument, but serve merely to modify slightly the value of n necessary for the crack to commence. Until a more exact formulation of the theory is available, it is not possible to state the value of n (the number of molecules involved in the start of a crack), but it is believed to be a small integer and to be itself subject to some variation of a statistical character.

GROWTH OF CRACKS

Powell and Gough[1] described in a general manner the way in which existing cracks caused stress release in the surrounding rubber and so caused interference of growth rates between neighboring cracks.

The degree of interference between two adjacent cracks will depend on the sizes of the cracks, their distance apart, and the amount by which they overlap. It is clear that the region around a crack in which the stress is appreciably released depends on the crack size. Because of this, a large crack is more likely to influence the growth of a small crack than the reverse.

Powell and Gough[1] also pointed out that the length and depth are roughly in unison, as would be expected if stress distribution is a major factor. Gould[9] has confirmed that the length/depth ratio is statistically constant in flexing samples. When two cracks join end to end, the length ceases to grow, presumably until the depth has reached the appropriate fraction of the length, and provided no other nearby cracks interfere.

To recapitulate, the suggestion is that a crack commences when a number of adjacent molecules carry the stress and are all attacked by ozone at the same time and the radicals or molecule ends at broken double bonds are pulled too far apart for recombination by kinetic motion. The same basic mechanism operates to cause extension of the highly stressed extremities of the crack and so ensures growth. At this stage the stress distribution largely controls the crack development.

This theory, is in effect, an improved version of Powell and Gough's theory in which crack formation is explained by a new hypothesis which may be considered to be a modification of Newton's theory of crack formation. The statistical character and dynamic nature of the process is emphasized.

CONSEQUENCES OF THE PROPOSED THEORY

(1) The theory explains the part played by stress in the production of visible cracks when ozone attacks stretched rubber and also why visible cracks do not form without the simultaneous action of stress and ozone.
(2) Stress release by cracks already formed reduces the probability of new cracks and ultimately settles the maximum crack density.
(3) Stress release due to crack development and joining ultimately causes a gradual reduction in the apparent number of cracks.
(4) A distribution arising from a continued product of probabilities (which are functions of time) tends towards a log.-normal distribution in time.

This provides a reason for the observed log.-normal distribution of rate of crack formation.

(5) The statistical uniformity of crack size and spacing and randomness of location of the cracks follows from the theory.

(6) More cracks will form and will start earlier in time with higher stress, since the required number of molecules (n) involved in the nucleus of a crack is less with a high than a low stress.

(7) Cracks grow preferentially through the regions of highest stress concentration (that is at the ends of the crack), because "n" is less for higher stress. Growth is materially affected by stress redistribution consequent upon the development of neighboring cracks.

(8) Increase of temperature increases crack density and causes cracks to occur at lower stresses because it increases the movement of the molecules and, hence, the number of different configurations of rubber and ozone molecules which occur in a given time. This increases the number of occasions when particular bonds are neighboring during that time. The increase in kinetic energy is not sufficient to cause appreciable recombination in spite of the applied stress.

These deductions are in accord with observed facts.

CONCLUSION

The technique of time lapse cine-micrography has enabled the cracking of rubber in ozone to be seen as a dynamic process. Further, the film so produced, recording as it does the complete life history of the cracks formed, enables their formation and growth to be studied.

The statistical nature of the crack formation period and the importance of stress release due to interaction between adjacent cracks is amply proved. Consideration of the detailed findings has suggested an improved theory of the physical development of ozone cracking. In particular, it explains the discrepancy between the number of visible cracks and the probable number of double bonds which may be attacked by ozone, and the part played by applied stress in the formation of cracks.

ACKNOWLEDGMENTS

The authors are indebted to many of their colleagues in the Dunlop Research Centre for assistance in this work. In particular they wish to thank (Miss) M. Davies for assistance in the analysis of the film, and S. B. Simcox and J.M. Hyabittle for collaboration in the production of the film. Acknowledgment is made to the Directors of the Dunlop Rubber Company Limited for permission to publish the paper.

SUMMARY

In order to study the development of cracks in stretched rubber exposed to ozone, a technique of time-lapse cinemicrography has been used. A film of crack formation and development at 30, 15 and 7½ per cent strain has been analyzed. In addition to giving a dynamic picture of the formation and growth of cracks, the film enables detailed measurements to be made throughout the whole process of cracking.

There are two main phases in the cracking of strained rubber by ozone, namely formation and growth. The results show that crack formation is

statistical in character, the rates being normally distributed with respect to the logarithm of time, and the crack location being random. Rate of crack growth is constant in time except when it is modified by crack joining or stress release due to the presence of neighboring cracks.

An attempt is made to co-ordinate these facts with the known effects of stress and the discrepancy between the number of available double bonds and the number of observed cracks. It is suggested that visible cracks commence only when several adjacent molecules carry the applied stress and, at the same time, neighboring double bonds in these molecules are attacked by ozone. This explains the relatively few visible cracks. The adequacy of this theory and its relation to earlier theories are discussed.

REFERENCES

[1] Powell and Gough, *Trans. Inst. Rubber Ind.* **21**, 102 (1945).
[2] Fry, "Probability and Its Engineering Uses", Van Nostrand & Co., New York.
[3] Newton, *J. Rubber Research* **14**, No. 3, 27 (1945); **14**, No. 4, 41 (1945); *Trans. Inst. Rubber Ind.* **21**, 113 (1945).
[4] Long, *Chem. Revs.* **27**, 437 (1940).
[5] Kendall, C. E., Dunlop Research Centre, Dunlop Rubber Co., private communication.
[6] Williams and Dale, *J. Applied Physics* **15**, 585 (1944).
[7] Powell and Gough, *Trans. Inst. Rubber Ind.* **21**, 102 (1945); Newton, *J. Rubber Research* **14**, No. 3, 27 (1945); **14**, No. 4, 41 (1945); *Trans. Inst. Rubber Ind.* **21**, 113 (1945); Leigh-Dugmore, *Rubber Age & Synthetics* **33**, 398, 442 (1952).
[8] Newton, *J. Rubber Research* **14**, No. 3, 27 (1945); **14**, No. 4, 41 (1945); *Trans. Inst. Rubber Ind.* **21**, 113 (1945); Leigh-Dugmore, *Rubber Age & Synthetics* **33**, 398, 442 (1952).
[9] Gould, E., Dunlop Research Centre, Dunlop Rubber Co., private communication.

OZONE FORMATION IN PHOTOCHEMICAL OXIDATION OF ORGANIC SUBSTANCES *

A. J. HAAGEN–SMIT AND C. E. BRADLEY

CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

AND M. M. FOX

LOS ANGELES COUNTY AIR POLLUTION CONTROL DISTRICT, LOS ANGELES, CALIFORNIA

Smog periods in the Los Angeles area are chemically characterized by a pronounced oxidizing effect, in the order of 0.6 p.p.m. (volume per volume), calculated as hydrogen peroxide, and usually measured by the liberation of iodine from neutral buffered potassium iodide solution.

The oxidizing action of smog can also be measured by the decolorization of dyes such as indigosulfonic acid or crystal violet. On the other hand, leuco dyes are readily oxidized to the corresponding colored compounds. A convenient smog indicator is colorless phenolphthalein, which is oxidized to phenolphthalein, giving a red color in alkaline solution. The intensity of the red color is a direct measure of the smog concentration. The rapid oxidation of cysteine and glutathione during smog periods is of interest, since the oxidation of sulfhydryl groups has been correlated with lachrymatory action[1].

It has been shown that this oxidizing effect of smog is due to the combined action of nitrogen oxides, peroxides, and ozone, counteracted by the reducing action of sulfur dioxide, which is present in concentrations of 0.1 to 0.2 p.p.m.

The presence of peroxides is explained by the photochemical oxidation of large quantities of hydrocarbons released into the air. In this reaction, nitrogen oxides play the role of catalysts[2]. The more puzzling fraction of the oxidant is the ozone, which reaches concentrations as high as 0.3 p.p.m., determined by rubber cracking experiments. The development of a quantitative rubber cracking test for ozone made it possible to follow this phenomenon during smog periods and to express the degree of cracking in concentrations of ozone which would give, under the same experimental conditions, the same typical cracking[3]. The time necessary for initial cracking of rubber during a smog period can be as short as 4 minutes, whereas on normal days this takes from 45 to 60 minutes. These cracking times correspond, respectively, to 0.3 and 0.02 p.p.m. of ozone.

The natural ozone concentration on the earth's surface is reported to be of the order 0.02 to 0.03 p.p.m. These values have been confirmed by the authors of this paper, using the rubber cracking test in unpolluted desert and beach areas. It is unlikely that additional ozone could be drawn from the higher atmosphere when the presence of inversion conditions characteristic for smog conditions prevents this free exchange. Further evidence against such a possibility is presented by the nearly complete absence of rubber cracking at night. This observation points to photochemical processes in the formation of the rubber cracking material.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 9, pages 2086–2089, September 1953. This paper was presented before the Division of Rubber Chemistry at its meeting in Los Angeles, California, March 31–April 2, 1953.

OZONE FORMATION WITH NITROGEN OXIDES

It was thought that the photochemical dissociation of nitrogen oxides, forming atomic oxygen and possibly ozone, could be the main cause of the rapid rubber cracking. When nitrogen oxides in concentrations of 0.4 p.p.m. in air were exposed for a few hours to sunlight, bent rubber pieces often showed typical ozone cracking. But when air purified by passing through activated carbon filters, or when pure oxygen was used in addition to nitrogen oxides, no cracking of rubber took place on exposure to sunlight. The laboratory air contained, therefore, enough impurities to give rubber cracking when nitrogen oxides were present.

Rapid rubber cracking, comparable to that observed during smog periods, was repeatedly observed during plant fumigation experiments, when hydrocarbons, nitrogen oxides, and sunlight were used, and this led to the suspicion that ozone might be formed in the photochemical oxidation of organic substances.

To study this reaction further, experiments were conducted in borosilicate glass flasks containing air with varying concentrations of organic substances and nitrogen oxides. The air was filtered through activated charcoal filters. Since

TABLE I

OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH 3-METHYLHEPTANE AND NITROGEN DIOXIDE IN SUNLIGHT

(Exposure time 3 hours; 2-liter reaction flasks)

3-Methylheptane (p.p.m.)	Nitrogen dioxide (p.p.m.)	Av. rate of ozone formation (p.p.m./hour)
70	0.4	None
3	0.4	0.4
1	0.4	1.0
0.1	0.4	1.3
1	0.1	0.2
1	0.02	None
1.4	None	None

these experiments simulated atmospheric conditions, no attempt was made to remove the water from the air, and later experiments showed that traces of water were essential for the reaction. Bent strips of rubber were suspended in the flasks before exposing them to sunlight. The rubber cracking obtained was compared with that given by known concentrations of ozone.

It was postulated that peroxides play a role in the formation of ozone, and branched saturated hydrocarbons were selected as test materials, since these substances readily yield peroxides on photochemical oxidation with nitrogen dioxide. When the reaction is carried out in the presence of rubber, no isolation of the peroxides is necessary, thereby avoiding the destruction of the most active primary oxidation products. Since the success of the experiment depends on a preferential oxidation of the rubber, a saturated hydrocarbon was chosen, rather than an olefin.

Using a concentration of 0.1 p.p.m. of 3-methylheptane and 0.4 p.p.m. of nitrogen dioxide in air, in a 2-liter flask, pronounced rubber cracking was observed in 1 hour, while in parallel experiments, using either one alone at the same concentration, no cracking was seen in 5 hours. Table I contains the data obtained with different concentrations of 3-methylheptane and nitrogen oxides. Photochemical formation of the rubber cracking material takes place only at

low concentrations of hydrocarbon, and a large excess of hydrocarbon completely inhibits the rubber cracking. Quenching action on photochemical processes has been observed frequently in other cases.

When the flasks filled with air containing 3-methylheptane and nitrogen dioxide were exposed to sunlight for several hours and bent rubber strips were subsequently introduced, heavy cracking was observed in the absence of light. The rubber cracking material is, therefore, stable. When the contents of the flask were passed through a ferric ferricyanide solution, the solution turned blue because of the presence of peroxides and nitrogen oxides. The rubber cracking material, however, was not absorbed. After passing through the solution, its presence can be demonstrated by rubber cracking and iodine release from potassium iodide solutions. This behavior indicates that the rubber cracking material is ozone, and its presence was confirmed by isolation from the reaction mixture by condensation.

TABLE II

OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH ORGANIC ACIDS, NITROGEN OXIDES, AND SUNLIGHT

Test acid	Concn. (p.p.m.) (V/V)	Nitrogen oxides (p.p.m.) (V/V)	Flask volume (l.)	Exposure (min.)	Av. rate of ozone formation (p.p.m./hour)
Formic	1	0.4	2	120	0
Acetic	1	0.4	2	120	0.1
Propionic	1	0.4	2	120	0.3
Butyric	1	0.4	2	120	0.5
Valeric	1	0.4	2	120	1.0
Caproic	1	0.4	2	120	1.0
Heptylic	1	0.4	2	120	1.0
Caprylic	1	0.4	2	120	0.8
Diethylacetic	1	0.4	2	180	1.0
Diethylacetic	0.1	0.4	12	5	0.8
Diethylacetic	0.1	0.4	12	6	1.3
Diethylacetic	0.1	0.4	12	20	1.2
Methylethylacetic	1	0.4	2	240	0.6
Pyruvic[a]	1	0.4	5	210	0.3

[a] At higher concentrations, rubber cracking was observed in absence of nitrogen oxides.

When the contents of a 12-liter flask of irradiated nitrogen dioxide (0.4 p.p.m.) plus 3-methylheptane (2 p.p.m.) in air were slowly drawn through a series of Shepherd absorption traps held, respectively, at −20°, −80°, and −180°C, the first two traps contained all the nitrogen oxides and peroxides. The rubber cracking material collected in the −180°C trap. This behavior on fractional condensation, the liberation of iodine from neutral potassium iodide solution, decolorization of crystal violet and indigo sulfonic acid solutions, and the typical ozone smell of the condensate from the −180°C trap established the presence of ozone.

The strong rubber cracking observed with 3-methylheptane and nitrogen dioxide in air seems to be a rather general phenomenon in the photochemical oxidation of organic substances, and the authors have observed this action with other hydrocarbons, as well as with their oxidation products—acids, aldehydes, and alcohols.

In a series of straight-chain organic acids, ranging from formic to pelargonic acid, the optimum effect after photochemical oxidation with nitrogen dioxide in air was found with the acids containing five to eight carbon atoms (Table II).

Formic acid gave no rubber cracking. Branched-chain organic acids also produced ozone in these experiments. For example, with diethylacetic acid at 0.1 p.p.m. in air and 0.4 p.p.m. nitrogen dioxide, in a 12-liter flask, definite rubber cracking was obtained in a 5-minute exposure to sunlight. The ozone formed was isolated by fractional condensation and identified as described in the case of 3-methylheptane.

In Table III the ozone formation in the photochemical oxidation of a miscellaneous group of substances with nitrogen oxides is given. No cracking

TABLE III

OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH ORGANIC COMPOUNDS, NITROGEN OXIDES, AND SUNLIGHT

Test material	Concn. (p.p.m.) (V/V)	Nitrogen oxides (p.p.m.) (V/V)	Flask volume (l.)	Exposure (min.)	Av. rate of ozone formation (p.p.m./hour)
Isobutane	1	0.4	2	180	0.2
n-4-Nonene	0.1	0.4	2	180	0.2
Mesitylene	1	0.4	2	240	0.9
Ketene	1	0.4	2	120	0.9
Diethyl carbinol	1	0.4	2	240	0.9
Methylpropyl carbinol	1	0.4	2	180	0.5
n-Butyraldehyde	0.1	0.4	2	210	0.4
n-Butyraldehyde	1	0.4	2	180	0.5

was observed in the absence of nitrogen oxides. No cracking was noticed in the presence of 0.4 p.p.m. of nitrogen oxides with acetone, acetonyl acetone, formaldehyde, carbon monoxide, isopropyl alcohol, methane, ethane, or propane.

In Table IV are listed oxidation experiments with different concentrations of nitrogen dioxide in air, while the concentration of the organic material, caprylic acid, was kept constant at 1 p.p.m. Optimum effect is noticed at concentrations which have been measured during severe smog.

TABLE IV

OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH CAPRYLIC ACID AND NITROGEN DIOXIDE IN AIR WITH SUNLIGHT

(Exposure time 1 hour; 2-liter reaction flasks)

Caprylic acid (p.p.m.) (V/V)	Nitrogen dioxide (p.p.m.) (V/V)	Rate of ozone formation (p.p.m./hour)
1	20	0.4
1	5	0.6
1	2	0.7
1	0.4	0.8
1	0.1	0.6
None	20	None
None	0.4	None

Table V lists rubber cracking data obtained with 10°C fractions of ethyl gasoline as source of hydrocarbon. The concentration of the gasoline fractions in air was 1 p.p.m.; the nitrogen oxide concentation was 0.4 p.p.m. In concentration of 0.1 p.p.m., when oxidized with 0.4 p.p.m. nitrogen dioxide in sunlight for 1 hour, the 70° to 80°C fraction gave rubber cracking corresponding to 0.2 p.p.m. ozone.

The ozone formation with gasoline fractions is attributed to their content of branched unsaturated hydrocarbons and olefins. Olefins which, on oxidation

with nitrogen dioxide and sunlight, yield aldehydes and acids of the proper chain length can be expected to contribute to the ozone formation. This was confirmed by the photochemical oxidation with 0.4 p.p.m. nitrogen dioxide of 0.1 p.p.m. *n*-4-nonene, whereby 1.4 p.p.m. of ozone were formed in 3 hours. The oxidation of *n*-4-nonene results in the formation of *n*-butyric and *n*-valeric acids and the corresponding aldehydes, all of which are active in ozone production.

A comparison of the ozone concentrations obtained in many of the photochemical oxidations with the concentrations of nitrogen dioxide and organic substances used shows that the amount of ozone formed is several times greater than could be theoretically developed from a stoichiometric reaction of the hydrocarbon and nitrogen dioxide. It was therefore concluded that ozone is formed in a chain reaction. The photochemical dissociation of nitrogen dioxide with sunlight provides a continuous source of atomic oxygen for this reaction,

TABLE V

OZONE FORMATION CALCULATED FROM RUBBER CRACKING WITH GASOLINE FRACTIONS (1 P.P.M) AND NITROGEN DIOXIDE (0.4 P.P.M.) IN AIR AND SUNLIGHT

(Exposure time 3 hours; 2-liter reaction flasks)

Gasoline fraction (b.p., °C)	Rate of ozone formation (p.p.m./hour)
0–40	0.2
40–50	None
50–60	None
60–70	0.6
70–80	0.9
80–90	0.4
90–100	0.3
100–110	0.4
110–120	0.4
120–130	0.4
130–140	0.4
140–150	None
150–160	None
160–170	0.2
170–180	0.2
Blank, NO_2 only	None

since nitrogen dioxide is regenerated through oxidation of nitric oxide by molecular oxygen. The formation of ozone is therefore dependent on the presence of oxygen. It has been shown that replacement of air with nitrogen completely suppresses the rubber cracking. It is postulated that in the chain reaction leading to ozone formation, peroxide radicals are formed which react with molecular oxygen to form ozone. After the peroxide radical has released one of its oxygen atoms, it may be reoxidized and can then react with molecular oxygen.

Intermediate steps in the reaction with oxygen might consist in the formation of HO_2 radicals, which subsequently react with a peroxide radical to give ozone. The fact that water must be present in these reactions lends support to the postulation of this intermediate step.

Ozone formation in the photochemical oxidation of organic material and its explanation parallels that of the ozone formation in the oxidation of inorganic substances such as phosphorus. Fischbeck and Eich, in 1938, in a study of the ozone formation with phosphorus and oxygen, gave evidence that this formation takes place through a chain mechanism involving the formation of phosphoric

oxides and peroxides[4]. In the case described in this paper, the alkyl radicals formed might serve in a similar way as oxygen acceptors.

OZONE FROM DIKETONES AND ALKYL NITRITES

To test the peroxide radical chain hypothesis in the formation of ozone, the photochemical oxidation of biacetyl was studied, since it is known that biacetyl, under the influence of light, easily forms free radicals. In this experiment, nitrogen dioxide is not necessary for the transfer of light energy, since biacetyl absorbs light in the visible range of the spectrum. Biacetyl, in concentration of 2000 p.p.m. in air in a 2-liter borosilicate glass flask, gave rapid rubber cracking. The contents of the flask were drawn through Shepherd traps held at −20°, −80°, and −180°C. After warming the −180° trap to −100°C while passing nitrogen through, the gas released decolorized crystal violet and indigo sulfonic acid solutions, liberated iodine from neutral buffered potassium iodide solution, did not affect ferric ferricyanide solution, and had the typical ozone smell. When passed over a rubber test strip, rubber cracking was observed within seconds. Traces of water are necessary in the formation of ozone, since thoroughly dried air and biacetyl failed to give rubber cracking.

TABLE VI

PHOTOCHEMICAL OZONE FORMATION FROM BIACETYL

Exposure (min.)	Ozone formed (p.p.m.) (V/V) Biacetyl (2000 p.p.m.)	Biacetyl (20,000 p.p.m.)
2	3	..
4	9	..
8	14	..
16	19	..
20	22	..
30	30	64
40	28	..
60	28	83
120	..	60
150	24	..
240	2	31
480	1	0

In the experiment using six 22-liter flasks in series, each containing 2000 p.p.m. biacetyl, the ozone formed was isolated by fractional condensation and its identity confirmed by R. Badger through infrared spectroscopic analysis.

The lowest concentration of biacetyl at which cracking of rubber could be observed without addition of nitrogen oxides was 40 p.p.m. This concentration is considerably higher than that of the hydrocarbons used in the photochemical oxidation with nitrogen dioxide. The main reason for this is probably the irreversible decomposition of biacetyl in light to products such as acetyl peroxide, peracetic acid, acetic acid, and formic acid. These do not form ozone under the influence of sunlight.

In separate 2-liter borosilicate glass flasks, samples of biacetyl in air were exposed to bright sunlight for varying periods of time. The contents of the flasks were then passed through a series of three Shepherd traps held at −100°C and then through a bubbler containing neutral buffered potassium iodide solution. The iodine released was titrated with 0.001 *N* sodium thiosulfate solution, and the ozone concentration calculated. The entire oxidizing effect

was due to ozone, since peroxides and other oxidants were effectively retained in the traps. Table VI shows that after 30 minutes the ozone concentration had reached a maximum concentration of 30 p.p.m.

When the biacetyl concentration is increased by a factor of 10, the maximum obtainable ozone concentration is increased by a factor of only 2.5. The observed ozone formation is, therefore, not directly proportional to the biacetyl concentration, but depends on side reactions, such as the reaction of the ozone formed with oxidation products of biacetyl and with biacetyl itself.

Bibutyryl, also a 1,2-diketone, gives rubber cracking and, therefore, ozone, when exposed to sunlight in the absence of nitrogen oxides. Ozone formation has been observed using the α-keto acid, pyruvic acid. The amount of ozone formed is considerably less than in the case of biacetyl, but can be readily demonstrated by the cracking of a bent piece of rubber suspended during or after irradiation in a flask containing pyruvic acid. As in the case of biacetyl, ozone formation can be observed with a concentration of 1 p.p.m. when 0.4 p.p.m. nitrogen dioxide is present. The expectation of ozone formation by compounds which upon oxidation would give rise to pyruvic acid was verified by exposing mesitylene in air with 0.4 p.p.m. of nitrogen dioxide to sunlight (Table III).

Rubber cracking without the addition of nitrogen oxide is also observed when butyl nitrite in a concentration of 0.1 p.p.m. is exposed to sunlight. It is known that in the absence of oxygen, alkyl radicals and nitrogen oxides are formed by the decomposition of butyl nitrite. The expectation that, in the presence of oxygen, ozone would be formed was confirmed by the rapid rubber cracking observed.

ECONOMIC AND HEALTH ASPECTS

In the photochemical oxidation with nitrogen dioxide and organic substances —hydrocarbons and their oxidation products—ozone is formed in concentrations as high as several parts per million. The concentration of the organic materials used in these experiments, as well as that of nitrogen dioxide, is of the same order as those found in the Los Angeles atmosphere during smog periods.

The Los Angeles County Air Pollution Control District found that in the processing, handling, and use of hydrocarbons, large quantities of hydrocarbons, in the order of 2000 tons, are emitted daily to the air, while simultaneously 250 tons of nitrogen oxides are released from combustion processes. Analyses of the smog air have shown the presence of 1 to 2 p.p.m. of hydrocarbons and 0.4 p.p.m. of nitrogen oxides[5].

The abnormally high ozone content of smog air and consequent severe rubber cracking during such a period is, therefore, readily accounted for by the ozone formed in oxidation reactions.

Cracked gasoline consists mainly of branched saturated hydrocarbons and olefins which are rapidly oxidized by nitrogen oxides in the presence of sunlight. In this oxidation irritating peroxides, acids, aldehydes, and ozone are formed[6]. The organic acids and aldehydes of proper chain length produce further quantities of ozone with nitrogen dioxide and sunlight.

The combustion of the organic material in the air is, therefore, a gradual one. During the shortening of the chain, many of the intermediates may function in turn as ozone producers. Peroxide radicals, appearing as intermediates in this degradation, are postulated to produce ozone through their reaction with molecular oxygen.

Under the meteorological and geographical conditions existing in the Los Angeles area, the release of hydrocarbons and nitrogen dioxide in this area could lead to ozone concentrations of several parts per million. Fortunately, its accumulation is limited by the following factors:

Action of reducing compounds, such as sulfur dioxide.

Decomposition by light.

Gradual degradation of the organic compounds to carbon dioxide and the formation of nonvolatile polymerization products.

Addition reactions with aromatic compounds and unsaturated hydrocarbons, such as acetylene and ethylene, which do not form ozone in the photochemical oxidation with nitrogen dioxide.

Oxidation of nitrogen oxides to nitric acid.

Removal of nitrogen dioxide by the formation of nonvolatile nitro compounds.

These reactions are responsible for the rapid decrease in ozone concentration toward evening when the photochemical regeneration of ozone has come to an end. During smog periods, the formation of ozone outweighs its destruction, and ozone concentrations of 0.2 to 0.3 p.p.m. have repeatedly been recorded. These concentrations are several times greater than the maximum level of 0.1 p.p.m. recommended for safe working conditions by the American Medical Association Council on Physical Therapy.

The abnormally high ozone concentrations found in the Los Angeles area during a smog period, formed, as shown, by the photochemical oxidation of hydrocarbons by sunlight in the presence of nitrogen oxides, present not only a health hazard but also a problem of considerable economic importance[7].

In view of the photochemical formation of ozone at ground level, the rubber industry, in planning its storage facilities, must consider not only the ozone already present in the air but also the potential sources of ozone, such as the simultaneous presence of hydrocarbons, their oxidation products, and nitrogen oxides. It has been found that the resultant ozone can be effectively removed through the use of activated carbon filters. When storage in the open air is necessary, the contamination of the area with gasoline vapors and nitrogen dioxide producing combustions, such as take place in the automobile, should be avoided.

SUMMARY

The formation of ozone through photochemical oxidation of alcohols, aldehydes, ketones, acids, and hydrocarbons, such as are present in gasoline, in the presence of small quantities of nitrogen oxides has been demonstrated. Ozone production without the addition of nitrogen oxides has been observed in the photochemical oxidation of biacetyl, bibutyryl, pyruvic acid, and butyl nitrite. The ozone produced in these reactions was identified by chemical and physical methods. The ozone formation is attributed to a peroxide radical chain reaction.

The release of large quantities of hydrocarbons to the air and the simultaneous presence of nitrogen oxides from combustion processes explains the relatively high ozone content, and consequent severe rubber cracking, in the Los Angeles area. These findings should be considered in planning rubber storage facilities.

In view of the irritating properties of the products formed by this photochemical oxidation, both hydrocarbons and nitrogen oxides should be considered as potential irritants when they occur simultaneously in the air at low concentrations.

REFERENCES

[1] Dixon, *Biochem. Soc. Symposia* (Cambridge, England), No. 2, 39–49 (1951).
[2] Haagen-Smit, *Ind. Eng. Chem.* **44**, 1342 (1952); Los Angeles County Air Pollution Control District, "Second Technical and Administrative Report on Air Pollution Control in Los Angeles County—1950–1951" (May 1952).
[3] Bradley and Haagen-Smit, RUBBER CHEM. & TECHNOL. **24**, 750 (1951).
[4] Fischbeck and Eich, *Ber.* **71B**, 520 (1938).
[5] Los Angeles County Air Pollution Control District, "Second Technical and Administrative Report on Air Pollution Control in Los Angeles County—1950–1951" (May 1952).
[6] Haagen-Smit, Darley, Zaitlin, Hull, and Noble, *Plant Physiol.* **27**, 18 (1952).
[7] Haagen-Smit, *Ind. Eng. Chem.* **44**, 1342 (1952).

CALCULABLE PROPERTIES OF TECHNICAL RUBBER MIXTURES *

E. SCHREUER

PHYSIKALISCHES INSTITUT DER TECHNISCHEN HOCHSCHULE, KARLSRUHE, GERMANY

REAL AND IDEAL MIXTURES

If real mixtures are understood to be those whose resulting properties can not be represented as the sum of the partial properties of their components, then technical rubber mixtures must be considered to belong in this group. This is apparent in the usual designation of the components of the mixture, which are differentiated as active additives and mere fillers. The concept of the activity of an added material is associated with the representation of a schematic change of the medium while a socalled filler is capable of changing the properties of the vehicle only through the participation ratio.

Actually, in most cases, there is no obvious relationship between the change in the technically important properties and the corresponding properties of the active components which effect the change; estimation, or projecting and controlling the properties of rubber mixtures is essentially empirical.

However, there are some physical values which, just as in an ideal mixture, can be calculated from the individual properties of the mixture components; for example, the density, when considered as the sum of the partial densities of the mixture components, agrees so well with the density of the final mixture that frequently in practice this comparison, in addition to other factors, serves to control the recipe. From this it must be concluded that, during the mixing process and during vulcanization, no significant volume change occurs nor any change of the internal energy which is always associated with it.

This conclusion has induced the author to draw some inferences with respect to an additivity also of those thermodynamic properties which are very closely related to the internal energy. These are the cubic expansion coefficient α, the specific heat C_p, and the compressibility $\varkappa$. An investigation of the thermoelastic constants involved in the Gough-Joule effect of a series of very different

$$\left(\frac{\partial \vartheta}{\partial p}\right)_s = \frac{J \cdot T \cdot \alpha}{\rho \cdot C_p} \tag{1}$$

ρ = Density
J = Thermal work equivalent
T = Absolute temperature
ϑ = Temperature
p = Pressure

rubber mixtures showed agreement, within experimental accuracy, between values of this effect experimentally determined and the values calculated according to the mixed-component rule[1].

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by (Miss) Leora E. Straka of the Research Library of the Goodyear Tire & Rubber Company from the *Kolloid-Zeitschrift*, Vol. 128, No. 3, pages 159–164, March 1952.

On the other hand, measurements (undertaken in connection with the problem of damping) of the compressibility of the same rubber samples showed deviations from the values calculated according to the mixed-component rule which exceeded by about ±10 per cent the accuracy of the measurements. This result was the reason for testing the entire system of the above mentioned thermodynamic quantities with respect to their additivity and for investigating the relationships of the deviations which were obviously still present.

EXPERIMENTAL PROCEDURE AND CALCULATION METHODS

The same apparatus was used for the determination of the density, expansion coefficient, and compressibility. It is essentially a brass container (volume about 9 cc.) for receiving the sample, and is provided with a ground cover. The cover is pressed on with stop-cock grease and fastened with three screws. In a hole of the cover there is a calibrated capillary (1 mm. ϕ) which is made pressure-tight with Araldit and cemented so that it is water-tight. After introduction of the sample, the vessel is closed and is filled with water under vacuum up to some mark on the vertical tube.

For the density measurement, the vessel is used in the same way as a pycnometer.

In the measurement of expansion coefficients, the container is placed in a water thermostat, and the volume change with temperature is measured by the displacement of the fluid meniscus in the protruding portion of the capillary. Expansion of the container and of the water is taken into consideration, in the usual manner, in the calculations.

In the determination of compressibility, the container is placed in a steel piezometer tube so that the capillary appears in the field of vision of two opposite glass windows. The sinking of the meniscus which occurs under pressure is measured by a low-power microscope, and the compressibility of the water is taken into account in the calculation. The pressure measurement is recorded on a technical manometer (15 atm. with 0.25 atm. divisions) mounted directly on the piezometer. A nitrogen flask with a reducing valve is used for producing and regulating the pressure.

Because of the low heat conductivity of the samples and the temperature dependence of the value to be measured, the exact determination of specific heat requires considerable expenditure for equipment. Since such an apparatus was not available, this quantity was calculated by a new but equally reliable method, based on the exact Thomson formula. If Equation (1) is solved for C_p then, on the right, only experimentally determinable quantities remain, which were obtained either during the investigation or from earlier measurements[1].

This indirect method has been used also for the determination of the specific heat of the medium (Perbunan); just as in the case of the direct calorimetric method, it should be regarded and evaluated as an experimental method.

The experimental errors for the values determined according to this method are less than 2 per cent throughout and those of the density are less than 0.1 per cent. The sum of the properties E_n of the mixture components and the resulting property $\overline{E}$ of the mixture always conform to the simple mixture component rule according to the relationship:

$$\overline{E} = \sum_n k_n E_n \qquad (2)$$

where k_n represents the portion of the material in volume per cent (in specific

cases also in weight per cent). In our case, then, the procedure has certain difficulties if the properties are not known for individual materials, or if they are known only approximately. On the basis of the previously mentioned control formulas, the densities of all the ingredients are sufficiently accurate. α, $\varkappa$ and C_p values for sulfur, carbon black (graphite) and inorganic additions are taken from tables. However, in the case of base rubbers and the numerous organic additives, resins, accelerators, plasticizers, and antioxidants, it is necessary to resort to specific measurements or evaluations. Additives which were present in the mixture in more than 1 volume per cent were, therefore, investigated separately; the properties of the residual additives were evaluated by taking into account their consistency, density, and group relationship. Because of their small contribution, errors up to 50 per cent do not play an important role. In many cases an average value is sufficient for all additives

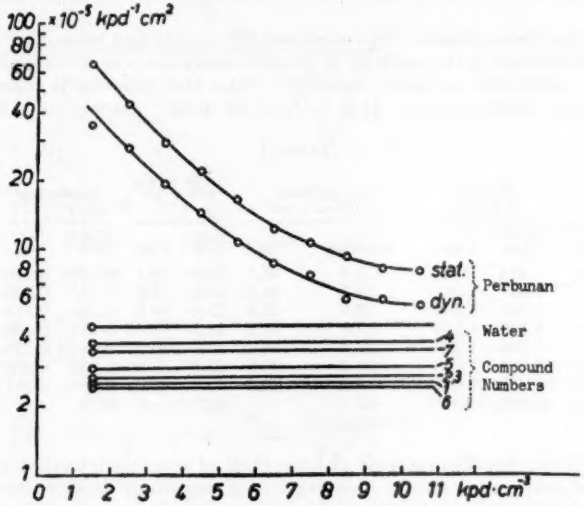


FIG. 1.—Compressibilities of various materials as a function of pressure.

of a definite class (as an example of such a value, the compressibility of all inorganic additives with the exception of sulfur is $1.5 \cdot 10^{-6}$ kpd^{-1}cm.^{2}) if the property of this class is of a smaller order of magnitude than that of the other ingredient.

RESULTS

Figure 1 shows the results of the compressibility measurements. In this case, measurements were made at intervals of 1 kpd cm.$^{-2}$ (kg·wt/cm.^{2}) up to 10 atmospheres inclusive.

As seen from the figure, the compressibility of the base rubber (Perbunan) is very strongly dependent on the pressure, and only at 10 atmospheres does it approach a published value ($54 \cdot 10^{-6}$ kpd^{-1}cm.^{2}) for natural rubber. Furthermore it depends on time, that is, the decrease of volume does not occur instantaneously but creeps to a final value which is attained only after a long time. The values of the curves designated as "dynamic" were read off im-

mediately after the compression stroke, while those designated as "static" were read off after about 2 minutes.

In addition, as might be expected, the curves depend on the prior compression load or recovery time of the sample. Therefore, they are not exactly reproducible and give only the picture of an "average" behavior. At any rate they show the following:

The composition of Perbunan is (at least in the sample under investigation) not completely homogeneous, but shows microscopic cavities which may be filled with gas. The occluded gas volume, although so small that it might not reduce the density to any noticeable extent, causes a large increase of the initial compressibility. Assuming that the occluded gas is under atmospheric pressure, the occluded volume can be roughly estimated from the initial compressibility to about $2\text{–}4 \cdot 10^{-3} V_0$. The gas cavities do not communicate with one another or with the surface; thus, they cannot be emptied by strong evacuation.

The time dependence of the compressibility points to a relaxation process; the volume change is the result of an internal resistance which can probably be correctly designated as *volume viscosity*. From this behavior it follows that rubber, even under uniform (that is, from all sides) compression, exhibits a

TABLE I

Material	Density (g. per cc.) Measured	Density (g. per cc.) Calc.	Compressibility $\times 10^6$ kpd^{-1}. cm.^{2} Measured	Compressibility $\times 10^6$ kpd^{-1}. cm.^{2} Calc.	Cubic expansion $\times 10^5$.°C^{-1} Measured	Cubic expansion $\times 10^5$.°C^{-1} Calc.	Specific heat cal./g.$^{-1}$ °C^{-1} Measured	Specific heat cal./g.$^{-1}$ °C^{-1} Calc.	Activity value
Mix 1	1.434	1.445	25.2	25.1	38.0	36.4	0.310	0.316	0.99
2	1.367	1.381	26.7	24.1	38.4	33.6	0.353	0.306	1.59
3	1.364	1.368	26.5	25.4	37.6	36.2	0.328	0.318	1.13
4	1.190	1.194	37.9	37.4	53.1	53.7	0.417	0.408	0.96
5	1.286	1.286	29.4	30.7	53.7	43.5	0.361	0.359	0.87
6	1.710	1.703	24.2	26.6	37.4	37.5	0.302	0.308	0.20
7	1.215	1.225	35.0	34.6	49.8	49.0	0.388	0.381	1.67
Perbunan	0.980	—	45 Extrapolated	—	65.0	—	0.55	—	—

phase shift between the pressure and the state of compression; that is, under periodic stress it must show a damping whose magnitude depends on the frequency of the stress cycle. According to previously unpublished measurements, this compression damping in the compounds investigated is of the order of magnitude of 2–10 per cent at about 20 hertzian units.

The measurements of the seven different rubber compounds showed that their compressibilities were all below that of water. They show neither a pressure dependence nor a noticeable time dependence. The average values are also included in Figure 1.

This result can be explained by the fact that, during the mixing process, the gas cavities of the raw rubber are for the most part milled out and are evacuated. It is very certain that the compressibility of the rubber is smaller in the mixture than in the crude state, and only here corresponds to the "true" compressibility of the material. An extrapolation of the measured values of the samples to 100 per cent Perbunan, with consideration of the remaining organic components, gives a compressibility of about $45 \cdot 10^{-6}$ kpd^{-1} cm^2. This value was used in the calculation with partial properties; a comparison with the measured values shows that it has been chosen too high rather than too low.

The results of the measurements and calculations of the compressibilities, as well as all the other properties, are assembled in Table 1. They apply to the same compounds which were used in the earlier investigation[1], and have been prepared according to the general formulation. It should be noted, how-

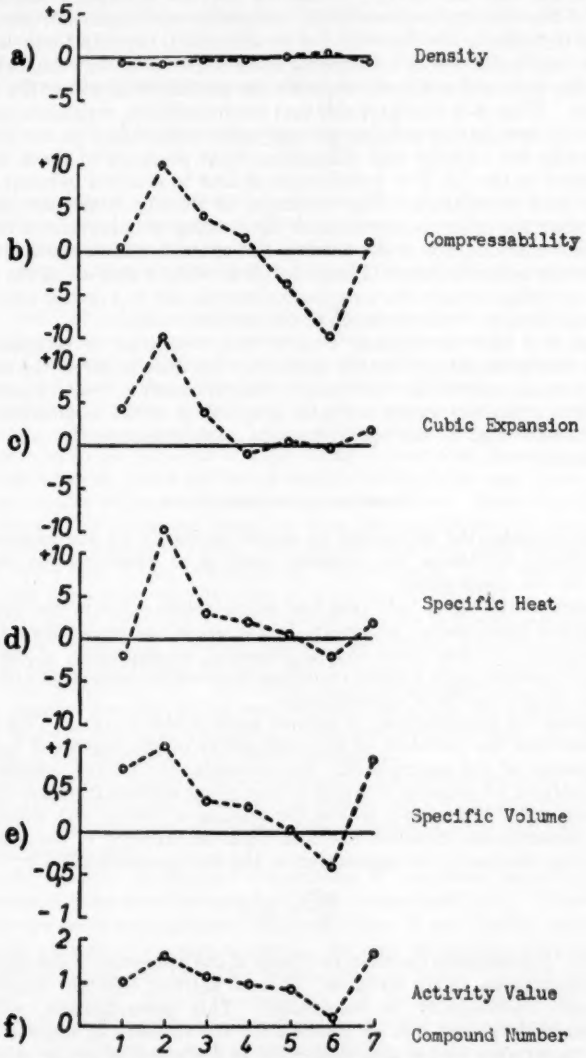


FIG. 2.—Relative deviation of the measured values from the calculated values of the specified material properties (in percentage).

ever, that sample No. 7 contains natural rubber instead of Perbunan as the base. A sample of this rubber was not available for individual investigation. With the exception of the reliable, available density value, all its properties were taken in the calculation to be the same as those of Perbunan. Figures 2 a–d record only the relative deviations between calculated and measured values of the density, compressibility, expansion coefficient, and specific heat. In order to facilitate the derivation of a relationship between these deviations, they are recorded above an optional sequence of the compound numbers (above an abscissa axis) and are connected with one another to illustrate the variation tendency. Thus it is unmistakable that compressibility, expansion coefficient, and specific heat have a common general trend with respect to the deviations. Individually the variance and different average positions of these deviations with respect to the $\Delta E/E = 0$ axis might at first be ascribed to errors of measurement and calculation. The variations of density which are essentially smaller than the other deviations show up as being unimportant in this trend.

If the variations, not of the density, but of the specific volume are plotted on a suitable magnified scale (Figure 2e), it is evident that all of the property changes investigated here show similar tendencies, and to a certain extent represent rough images of the deviation of the specific volume.

Thus, it is now immediately evident why the earlier investigated elastothermal constants behaved purely additively (at least as far as the measuring accuracy would permit this conclusion. This constant is $\sim \alpha/\rho \cdot C_p$; the deviations occur in approximately the same proportions in the denominator and in the numerator and in the same direction and, consequently, are mutually compensated.

POSSIBLE INTERPRETATION

If we consider the deviations as caused primarily by the experimentally found volume variations, the question arises as to whether these can be explained by the composition.

Volume variations of both plus and minus values occur in real mixtures in the solid and liquid state. In general, in the case of aggregates there also occur changes of the van der Waals linkage force and, consequently, of the internal pressure; therefore, such volume variations as a rule are associated with heats of reaction, which may be of opposite sign.

Likewise the nonadditivity of specific heats is also known. This is understandable from the variation of the multiplicity of the degrees of freedom at every change of the aggregation. For example, the partial specific heat of nonelectrolytes on solution in water or any other solvent increases with their concentration[2]. The same is true of the swelling of rubber with water[3].

If a material has an active effect on a partial property of the medium, its activity can frequently be represented to the first approximation by:

$$\frac{\Delta E}{E_0} = K \cdot c \tag{3}$$

where $\Delta E/E_0$ represents the relative change of the properties of the medium and c the concentration of the additive. K is an activity constant which may be determined theoretically or empirically. This generalization, which was theoretically developed first by Einstein for the viscosity of suspensions, is of general importance and is also applicable to the effect of active additions to rubber mixtures.

For example, Leontein[4] described a quantitative investigation of the mentioned regularity with respect to the effect of activated carbon on the magnitude of the elastic modulus. But even an earlier investigation showed that there was an almost proportional increase of the elastic modulus with the sulfur concentration[5].

If it is assumed in our case that the effective additions are essentially sulfur, carbon black, and active silicic acid, and if their activity is evaluated by the sum of their relative concentrations over that of the material which is to be activated, then the quantity corresponding to the right side of the Equation (3):

$$a = \frac{k_1 \cdot c_{\text{sulfur}} + k_2 \cdot c_{\text{carbon black}} + k_3 \cdot c_{\text{silicic acid}}}{c_{\text{Perbunan}}}$$

may be expected to be a measure of the desired change of the partial properties of the medium. The preponderant effectiveness of the sulfur is experimentally taken into consideration by the fact that the ratio of $k_1 : k_2 : k_3$ is selected as 100:1:1. The c's are the participation ratios of the materials in percentage by volume.

If the "activity value" a is plotted above the respective samples (Figure 2 f), the characteristic plot is again obtained. This shows that, for the properties investigated, the real mixtures deviate from the ideal mixtures, which are considered proportional to the concentration of active additives.

The stepwise increase, noted here, of the volume, expansion coefficient, specific heat, and compressibility, when active ingredients are added has a striking parallel to the behavior of supercooled liquids or of glasses in their so-called transformation phase (softening range); in this latter case these properties undergo similar changes with increasing temperature[6]. Since these changes are the result of an increasing deviation from the arrangement in the original network (which in liquids must not be considered as a crystalline arrangement), they can, according to our investigations, be attributed to an increase of the disorder with increasing concentration of the active ingredient.

Actually, such a conclusion is very plausible. As is known, thermoelastic and x-ray photographic evidence of localized anisotropy becomes increasingly difficult as the concentration of filler and the degree of vulcanization of the rubber mixture is increased. The most simple explanation is that the high degree of disorder occuring at the vulcanization temperatures is more strongly fixed and is more strongly "preserved" at normal temperatures, the stronger the linkage of the network by the active additives.

The significance of the undoubted regularities found here lies in the fact that it permits the relationship of many technically important properties which ordinarily are estimated and evaluated only empirically, with well defined and exactly specified values.

Thus, for example, in Figure 3 the softness W, measured according to the DVM standard, have been compared with the compressibility $\varkappa$. The data are plotted for the seven samples as a "function" (one of any usable parameters) of the total content of organic material. As may be seen at once from the value of the ordinates, the following relationship holds true for both properties (exception: Sample 2): $W = f(\varkappa \text{ constant})$. It should be noted that the correlation is found only for the calculated and not for the measured compressibilities. Since the softness as well as compressibility depend also on the elastic modulus E (or on the Poisson value μ), it may be assumed that the deviations

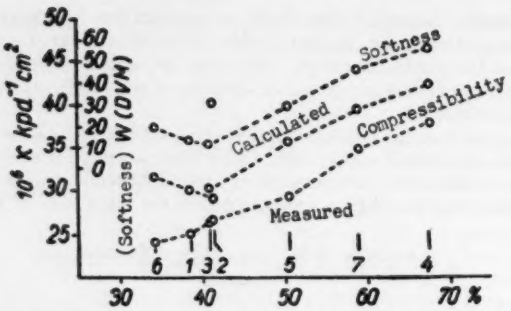


FIG. 3.—Softness W and compressibility κ of several rubber mixtures as a function of the total content of organic material. The calculated κ values are shifted up 5 units for better visibility.

are compensated here in the same way as the deviations of the values α and C_p in the example of the thermoelastic constants.

If this tentative and only heuristic relationship holds true for a larger range of materials than was available here, then such deviations from the group behavior, as in the case of Sample 2, are suitable for differentiating the physical effect of the so-called plasticizer. For the plasticizing effect can occur both as a result of an increase of the compressibility as well as through the decrease of the elastic modulus.

The latter case is understood then as favoring chain slipping by a decrease of the internal frictional resistance. That this is the situation with respect to Sample 2 is obvious from the above mentioned measurements of the internal friction (the so-called compression viscosity), which gave a considerably smaller value for this sample than for all the other samples.

SUMMARY

As a very enlightening example of nonideal material mixtures, technical rubber compounds show deviations from the additivity of thermodynamic and elastomechanical measured quantities which are to be expected according to the rule of mixed components.

The deviations have an intrinsic relationship, and bear a relation to the concentration of the so-called active additives.

ACKNOWLEDGMENT

These investigations were carried out in the Physical Institute of the Technical High School at Karlsruhe. I extend my sincere appreciation to Professor Chr. Gerthsen, for making possible the investigation by access to the facilities of the Institute and the encouragement lent by his constant interest.

REFERENCES

[1] Schreuer, *Kolloid Z.* **124**, 176 (1951).
[2] Bennewitz and Kratz, *Physik-Z.* **37**, 496 (1936).
[3] Vieweg and Gottwald, *Kunststoffe* **30**, 138 (1940).
[4] Leontein, *Trans. Inst. Rubber Ind.* **28**, 27 (1952).
[5] Hauck and Neumann, *Z. Physik. Chem.* (A) **182**, 265 (1938).
[6] See the description by Eucken, "Textbook of Physical Chemistry", II, 2, pp. 895 f.

NONLINEARITY IN THE DYNAMIC PROPERTIES OF VULCANIZED RUBBER COMPOUNDS *

W. P. Fletcher and A. N. Gent

British Rubber Producers' Research Association, Welwyn Garden City, Hertfordshire, England

INTRODUCTION

It has been noted by many investigators[1] that measured values of the dynamic properties of rubber loaded with mineral fillers show a variation with the amplitude of the dynamic strain to which the rubber is subjected. In a previous paper[2] attention is drawn to these effects and to the consequent difficulty in specifying the dynamic properties of such rubbers for engineering applications necessitating close tolerances.

More recent work by Waring[3] and by Gui, Wilkinson, and Gehman[4] has attempted to study these changes more systematically, and possible explanations have been discussed. In the latter work it is noted that the nonlinearity of dynamic modulus is most marked in compounds containing reinforcing fillers. The present investigation was undertaken in order to learn more about the relationship of this nonlinearity with other properties of the vulcanizates.

The fact that dynamic modulus at low amplitudes of vibration is sensitive to prior vibration at a high amplitude has been noted in the previous paper[2] for a natural-rubber tread compound. Gui, Wilkinson and Gehman[4] have reported a similar result for GR-S tread stocks. The initial values are slowly recovered on resting and, in the present paper, attention is drawn to the effect of temperature on this recovery.

Natural rubbers reinforced by other polymers in place of the conventional fillers[5] form an interesting new class of materials. It is of interest to examine such rubbers from the viewpoint of conformity or otherwise with the pattern of dynamic behavior found for rubbers reinforced with conventional fillers.

APPARATUS AND METHOD

The equipment for subjecting rubber test-pieces to a simple harmonic vibration, and the methods of measurement and analysis of the dynamic properties have been described previously[2]. The apparatus comprises briefly an electromagnetically excited resonance-type vibrator straining four rubber test-pieces in simple shear. Excitation is effected by the amplified output of a calibrated low frequency oscillator and the amplitude of the vibrating system is measured either directly, using a calibrated microscope, or for very low amplitudes by a photoelectric pickup and oscilloscope. From measurements of the resonant frequency and amplitude of vibration and from a knowledge of the amplitude of the applied sinusoidal force and the mass of the vibrating system, we may calculate (by making the usual assumption of linear theory) the stiffness and viscous coefficient of the rubber components and, hence, by reference

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 5, pages 266–280, October 1953.

to the dimensions of the test-pieces, the corresponding shear modulus and viscosity. The test pieces consist of rubber cylinders one inch in diameter and 0.25 inch in height, bonded to metal end plates. Four test-pieces are molded and tested together, and by altering the separation of the clamped metal end plates, it is possible to place the four test-pieces in a state of static shear strain while exerting no net force on the moving system, opposite mountings being strained in opposite senses. In the experiments described below, the test-pieces used were based on a standard pure-gum compound, containing 3 per cent sulfur and 0.5 per cent mercaptobenzothiazole accelerator, into which were incorporated 10, 20, 30, 40, and 50 parts by volume per 100 parts of rubber of the following fillers: MPC black, HAF black (Philblack-O), lampblack, FT black (P-33) and colloidal china clay.

THE ATTAINMENT OF EQUILIBRIUM

Test-pieces of a compound containing 20 parts by volume of MPC black were clamped in position ready for testing, and left for 48 hours to recover from any straining caused in inserting them in the test fixture. The modulus was then measured at a low amplitude of vibration, 0.04 per cent, and did not change measurably after several minutes of vibration. The test-pieces were then vibrated through an amplitude of 2.87 per cent shear, the modulus being measured as quickly as possible after the start of this vibration, and at intervals thereafter. The first measurement of modulus gave a value considerably lower than that obtained at the low amplitude, and the modulus decreased further with time as the vibration was continued. However, an equilibrium value was quickly attained and, after one and a half minutes, the further changes in the measured modulus values were small. Waring[2] has drawn attention to the fact that this decrease of modulus is, at least in part, due to a breadkown of the carbon structure and not to a temperature rise on vibrating, by making parallel measurements of electrical conductivity. As reported previously[3], under extreme experimental conditions a rise in temperature of about five degrees was measured. It is considered that the effect of an increase of temperature due to working will be small.

In the tests described below, measurements have been made two minutes after the commencement of vibration of the relevant amplitude, and it is felt that the error involved in taking this value for the equilibrium will be negligible.

RECOVERY FROM PREVIOUS VIBRATION AT A HIGH AMPLITUDE

After vibration for eight minutes at 2.87 per cent shear amplitude, the amplitude of vibration was reduced to a low level, 0.04 per cent shear, and the modulus measured as quickly as possible and at intervals thereafter. In the first few minutes a rapid increase in the modulus was observed, the recovery then becoming much slower. The original low-amplitude modulus value was substantially attained after 24 hours, the temperature throughout being 20° ± 2° C.

The temperature was then raised to 50° C and, after approximately an hour, the low amplitude modulus was measured, after which the test-pieces were subjected to a vibration of 2.87 per cent shear amplitude for some eight minutes. Immediately on cessation of this high amplitude vibration, the modulus was measured at the previous low vibration-amplitude and the recovery again followed with time. The changes of modulus were similar to those observed

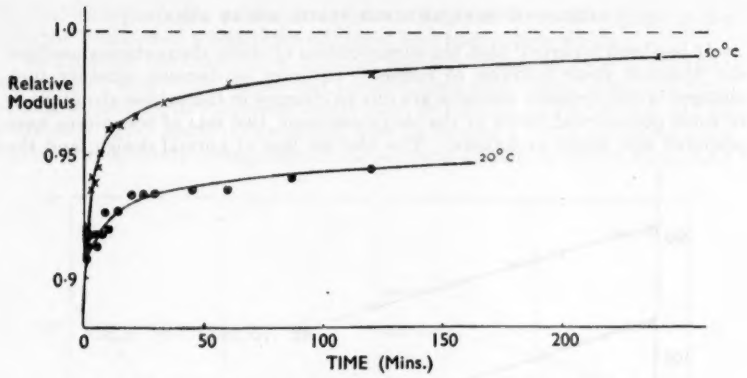


FIG. 1.—Plot of modulus relative to initial low-amplitude modulus against time from cessation of high-amplitude vibration.

at a temperature of 20° C, the initial rapid increase of modulus, however, being considerably larger.

The original low amplitude modulus at a temperature of 50° C was lower than that at 20° C and, in order to compare the recovery of modulus at the two temperatures in Figure 1, the modulus values are portrayed relative to the initial low amplitude modulus at the relevant temperature. The curves obtained are similar, but clearly not of a simple form, and the higher temperature is seen to cause a greater recover in the early stages.

DEPENDENCE OF THE DYNAMIC SHEAR MODULUS ON THE AMPLITUDE OF VIBRATION

EFFECT OF VOLUME LOADING AND TYPE OF FILLER ADDED

The test-pieces were allowed to rest in the test-fixture for 24 hours prior to testing to allow recovery from any accidental straining involved in clamping them. The shear modulus and viscosity were then measured initially at a low amplitude of vibration and, as the amplitude of vibration was increased, the changes of the dynamic properties were followed. The dependence of the modulus on the vibration amplitude for a vulcanizate containing various amounts of MPC black is shown in Figure 2.

A family of curves similar to those shown in Figure 2 for MPC black were obtained for the other types of carbon black studied and also for a vulcanizate containing colloidal china clay, although in this case the general shape of the modulus-amplitude of vibration curves is slightly different. The variations in the shapes of the modulus-amplitude curves between different fillers were comparable to the limits of accuracy of the measurements. In Figure 3 representative curves of the various fillers are presented, and the striking similarity in behavior of compounds containing different fillers is clearly shown.

It would appear that the shape of any curve is determined by the value of modulus at any single amplitude, over a wide range of conventional fillers.

EFFECT OF SUPERIMPOSED STATIC SHEAR STRAIN

It has been reported[2] that the superposition of static shear strains modifies the dynamic shear modulus of rubber. In order to discover whether such changes of the dynamic modulus are due to changes in the rubber structure or to some geometrical factor of the shape assumed, two sets of test-pieces were prepared and tested as follows. The first set was of normal design, and the

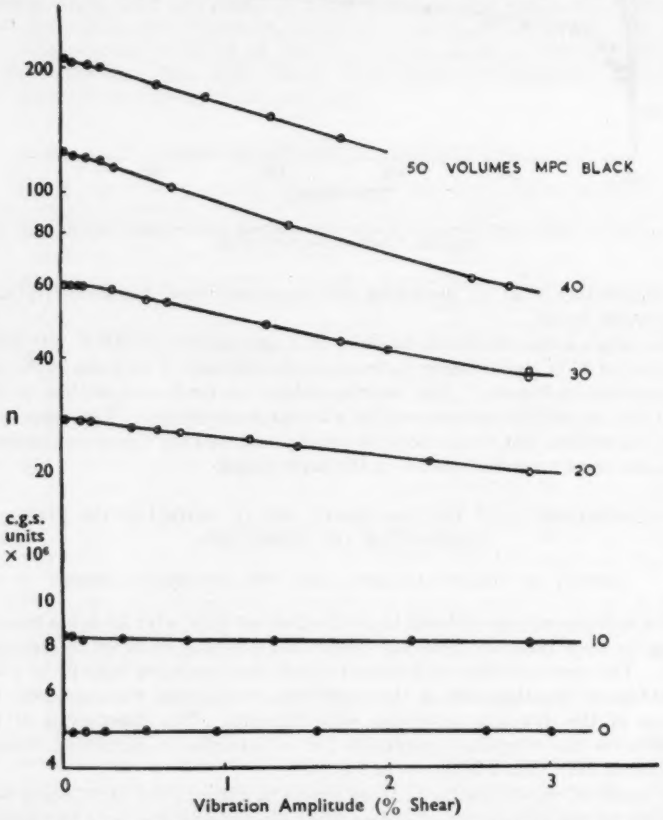


FIG. 2.—Variation of dynamic modulus with amplitude of vibration for compounds containing MPC black.

variation in dynamic modulus with superimposed static shear strain up to 20 per cent shear was studied.

The second set were molded to give skew cylinders having the same perpendicular height and diameter as the first, but skewed to the approximate shape of normal cylinders under 20 per cent shear strain. These were tested similarly, and at 20 per cent shear strain they appeared as right cylinders. The two tests showed similar variations of modulus with static shear strain, indicat-

ing that changes in the rubber structure are responsible for the change of the dynamic modulus of a test-piece subjected to a static shear strain.

In Figure 4, the variation of dynamic modulus with amplitude of vibration is displayed, with 0 and 30 per cent superimposed static shear strain, for compounds containing 20 volumes of lampblack, 20 volumes of Philblack-O and 28 volumes of MPC black. The broken lines in Figures 4 and 5 are copied from Figure 2 to facilitate comparison of the modulus-amplitude curves considered

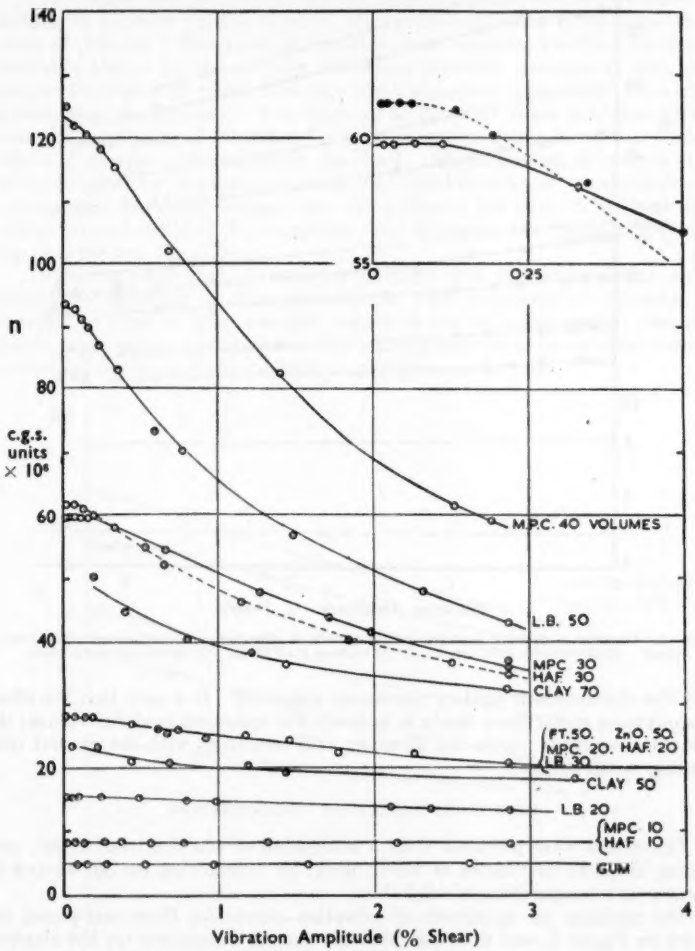


FIG. 3.—Variation of dynamic modulus with amplitude of vibration for compounds containing various fillers; channel black (MPC), lamp black (L.B.), furnace black (HAF), P-33 thermal black (F.T.), clay, zinc oxide, and also an unfilled pure-gum compound. The inset shows, on a larger scale, the initial parts of the curves for 30 parts of MPC black and for 30 parts of HAF black.

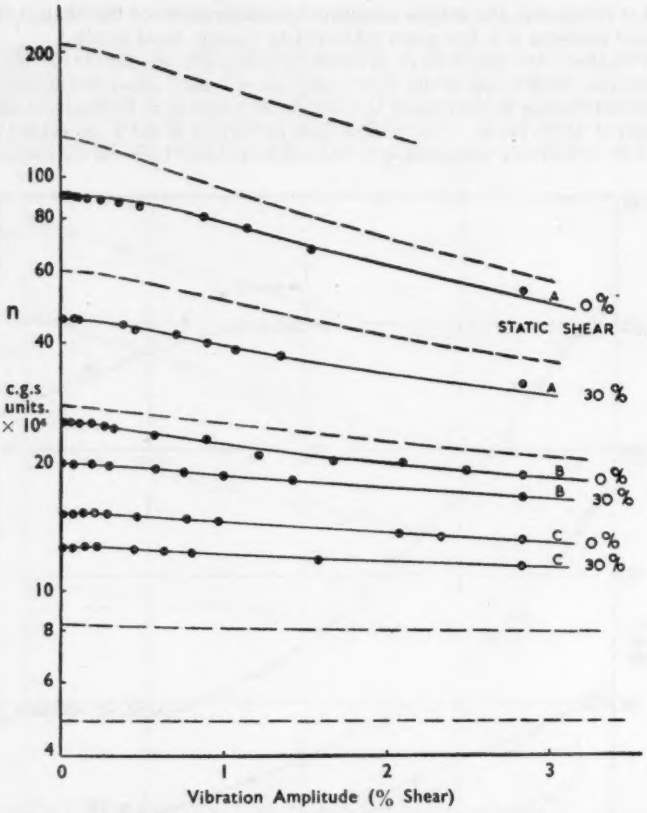


FIG. 4.—Variation of dynamic modulus with amplitude of vibration and superimposed static shear strain. A: 28 volumes MPC black. B: 20 volumes HAF black. C: 20 volumes lamp black.

with the characteristic pattern previously observed. It is seen that the effect of applying a static shear strain is to lower the measured modulus values; the modulus amplitude curves are however, still consistent with the general relationship noted earlier.

EFFECT OF DEGREE OF VULCANIZATION

Test-pieces were prepared from a compound of the tire-tread type[6], containing 28 parts by volume of MPC black, by vulcanizing for 30, 45 and 90 minutes at a temperature of 141° C.

The modulus vs. amplitude of vibration curves for these test-pieces are shown in Figure 5, and it is seen that the sample vulcanized for the shortest time showed a greater fall of dynamic modulus than is consistent with the value of zero-amplitude modulus obtained. The effect was confirmed in measurements on other grossly undercured filled compounds, and is in agreement with

results recently reported on an unvulcanized GR-S tread compound[4]. However, for reasonable degrees of vulcanization the modulus-amplitude curves obtained are of the same general character as those previously described. This was confirmed for compounds containing other accelerators and various sulfur-accelerator ratios.

EFFECT OF SOFTENER

Test-pieces were prepared in the tire tread compound referred to above containing 28 parts by volume of MPC black, with and without the addition of 4 parts of pine tar. The value of dynamic shear modulus was found to be considerably higher for the samples containing pine tar, presumably due to the greater facility with which a carbon black structure was able to form in the presence of the softener. The decrease of dynamic shear modulus with increasing amplitude of vibration for both compounds was however, in accord with the general pattern already described. Measurements of tension stress-strain properties of similar samples showed that below 5 per cent elongation the vulcanizate containing softener was the stiffer of the two. The stress-strain curves crossed at about this elongation, and thereafter the vulcanizate containing pine tar was the softer.

It thus appears that, for compounds filled with the conventional particle fillers, the variation of dynamic modulus with amplitude of vibration is a function of type of filler, amount, degree of vulcanization within reasonable limits, static strain, and presence of plasticizer only in so far as these variables determine the level of the modulus at any given amplitude.

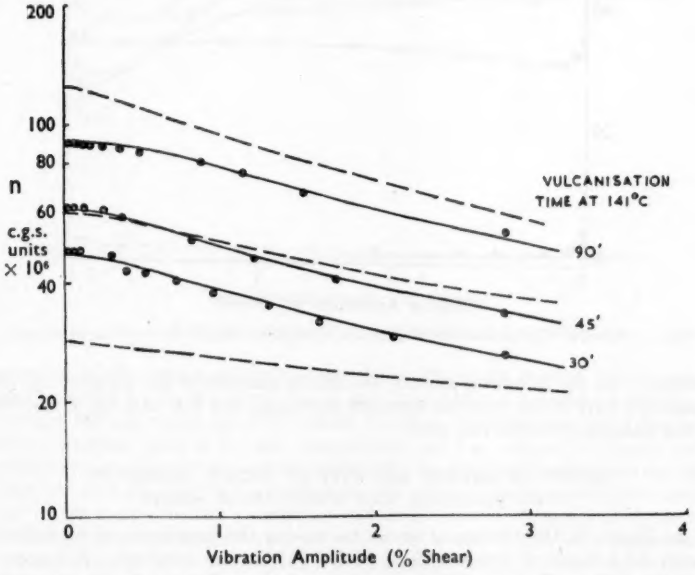


FIG. 5.—Variation of dynamic modulus with amplitude of vibration for three states of vulcanization of compound containing 28 volumes MPC black.

THE CORRESPONDING CHANGES IN DYNAMIC VISCOSITY

THE EFFECT OF FREQUENCY OF VIBRATION

Within the small frequency range available with the present test machine (20 to 120 c.p.s.), no measurable change of dynamic modulus with frequency at small or large amplitudes of vibration could be observed with the compounds considered. However, as previously reported[2], the dynamic viscosity was found to vary with frequency according to a law of the form $\eta \propto \omega^c$, where c varied between -0.72 and -0.95 depending on the amount of filler incor-

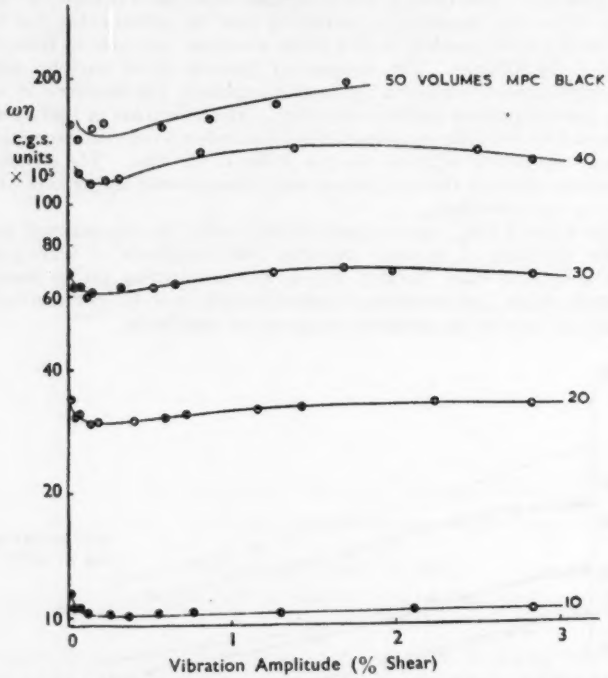


FIG. 6.—Variation of product $\omega\eta$ with amplitude of vibration for compounds containing MPC black.

porated. In the following section we discuss changes of the product $\omega\eta$, (the imaginary part of the complex dynamic modulus) and the ratio $\omega\eta/n$, the ratio of the imaginary to the real part.

EFFECT OF AMOUNT AND TYPE OF FILLER, DEGREE OF VULCANIZATION, AND STATIC SHEAR STRAIN

In Figure 6, the change of $\omega\eta$ on increasing the amplitude of vibration is shown for a series of compounds of varied MPC black content. It is seen to pass through a minimum at an amplitude of the order of 0.1 per cent shear, followed by a slight rise on increasing the amplitude. Similar families of

curves were obtained for the other fillers used. The increase of $\omega\eta$ on increasing the loading of a given filler is of a similar order to the corresponding increase of dynamic modulus n and it is, therefore, convenient to use the ratio of these two quantities $\omega\eta/n$ for comparisons between compounds and test conditions. The ratio $\omega\eta/n$ is tan δ, the tangent of the angle of mechanical loss, and measures the phase lag of deformation behind force when rubber is subjected to a sinusoidal force. Quantities closely related to tan δ are the ratio of successive amplitudes of a free vibration ($\propto$ tan δ) and the dynamic magnifier of a system comprising a mass and a rubber spring. The dynamic magnifier is the ratio of the resonant amplitude of such a system to the de-

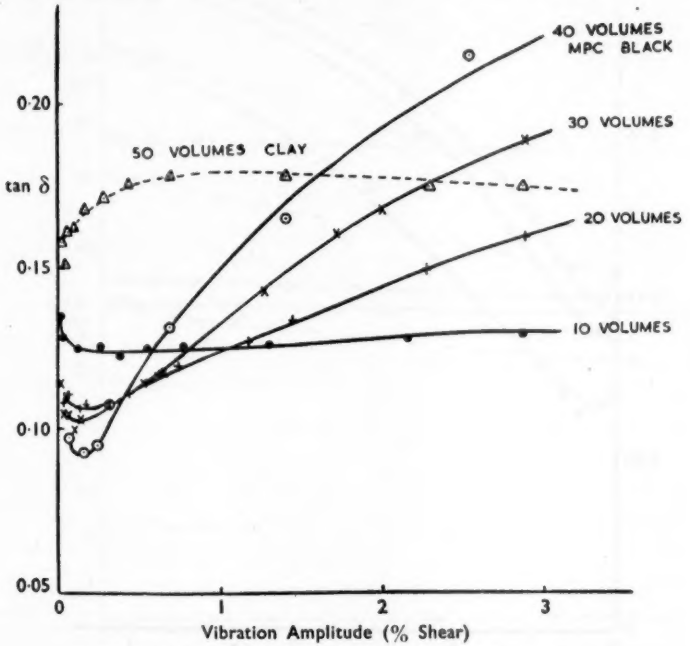


FIG. 7.—Variation of loss factor (tan δ) with amplitude of vibration.

formation of the spring element alone under the same applied force, and is equal to 1/tan δ. In Figure 7, tan δ has been plotted against amplitude of vibration for the series of MPC black loadings discussed earlier. For low volume loadings, that is, for soft compounds, tan δ is seen to be largely independent of the vibration amplitude, while the loadings required to obtain high values for modulus lead to a considerable rise of tan δ on increasing the amplitude. This is presumably a reflection of the decrease of dynamic modulus observed for these compounds under these conditions. When high proportions of nonreinforcing fillers are added, a general high value for tan δ is obtained throughout the amplitude range, as shown by the dotted curve of Figure 7, representing measured values for a compound containing 50 volumes of clay.

The application of a static shear strain on which vibration at increasing amplitude was superimposed was found to raise the measured values of tan δ at low amplitudes, while not appreciably affecting those at high amplitudes.

It was found that the position of these curves depends on the degree of vulcanization of the compound, and in Figure 8 typical results obtained for the tire tread compound referred to above are given. The curves are displaced

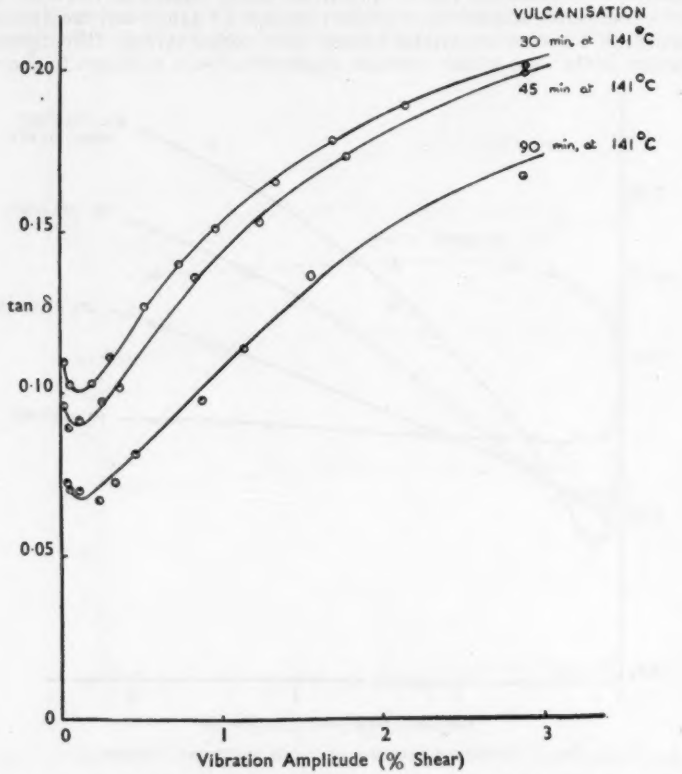


FIG. 8.—Variation of loss factor (tan δ) with amplitude of vibration for three states of vulcanisation of compound containing 28 volumes of MPC black.

towards lower values of tan δ on increasing the vulcanization time toward that giving a maximum value for dynamic modulus, and the vulcanization times giving minimum values to tan δ and the vulcanization times yielding maximum values for dynamic modulus were found to coincide for the series of compounds studied. In compounds of approximately equivalent modulus values in the tire tread modulus region, those based on fillers of low reinforcing power cured to minimum tan δ had values of tan δ which were high throughout the amplitude range, whereas those based on highly reinforcing fillers had lower tan δ

values at low amplitude, rising sharply with increasing amplitude to exceed the values shown by the former compounds.

RUBBER COMPOUNDS WITH POLYMERIC STIFFENING AGENTS

In contradistinction to the particle type fillers considered hitherto, compounds reinforced with long-chain polymers obtained in the manner described

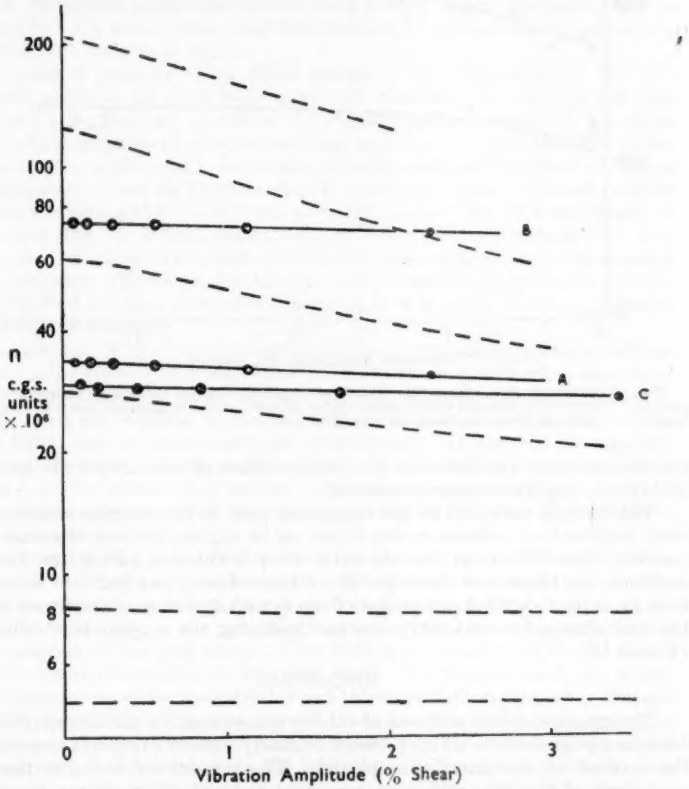


FIG. 9.—Variation of dynamic modulus with amplitude of vibration for three polymer-stiffened compounds. A: compound stiffened with cyclized rubber, B: with polymethyl methacrylate (chemically combined). C: with polymethyl methacrylate (mixed).

recently[5] show considerably less nonlinearity in their dynamic properties. In Figure 9 full-line curves, the modulus is plotted against the amplitude of vibration for two rubber-methyl methacrylate compounds of the mixed and chemically combined types and for a rubber cyclized-rubber compound, the dotted lines showing for comparison the behavior of MPC black-filled compounds. It is seen that the polymer-reinforced materials show a much smaller change of modulus with increasing amplitude of vibration than compounds con-

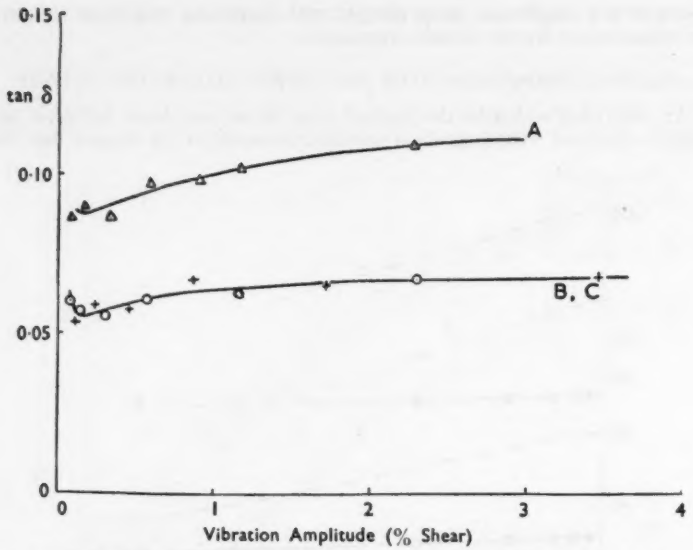


FIG. 10.—Variation of loss factor (tan δ) with amplitude of vibration for three polymer-stiffened compounds. A: compound stiffened with cyclized rubber, B: with polymethyl methacrylate (chemically combined). C: with polymethyl methacrylate (mixed).

taining conventional fillers for equivalent values of zero-amplitude modulus, within the amplitude range considered.

The form of variation of the imaginary part of the complex modulus, $\omega\eta$, with amplitude of vibration was found to be similar to that observed with particle fillers (Figure 6), but the ratio of $\omega\eta$ to the real part of the dynamic modulus, the tangent of the angle of mechanical loss, was found to be smaller than for a particle filled compound of the same value of zero-amplitude modulus, and changed considerably less on increasing the amplitude of vibration (Figure 10).

DISCUSSION

The increase of the stiffness of rubber consequent on the incorporation of fillers is a phenomenon which presents radically different features according to the method of examination employed. The present work shows that the magnitude of this filler stiffening, measured at small deformations, is reduced significantly by extremely small deformations of the rubber. Gui, Wilkinson, and Gehman[4] have pointed out the similarity between the nonlinear vibration characteristics of rubber and the non-Newtonian flow properties of disperse systems, and have suggested a bond-breaking mechanism to account for the nonlinearity. The experiments of these workers did not show any evidence of a limiting low amplitude below which nonlinearity was absent, a limit (yield point) which is usually found in non-Newtonian flow. The present experiments, which include measurements at amplitudes below those used by Gui, Wilkinson, and Gehman, do in some cases suggest the presence of such a limiting amplitude. The early part of the modulus vs. amplitude curves for 30-

volume loading of MPC and HAF blacks, shown in the inset of Figure 3, exemplify this suggestion, but more accurate measurements at low amplitude would be required to establish this point quantitatively and set values for the limiting amplitude. The slope of the modulus *vs.* amplitude curve, when plotted against amplitude, would relate closely to the frequency distribution of bond strengths, where strength is expressed in terms of the strain amplitude necessary to break a given bond, such a hypothetical distribution for the MPC or HAF 30-volume compound would have a very broad maximum, with a sharp fall to a low or zero frequency below about 0.1 per cent strain, and a long tail in the high amplitude region.

The marked memory effect which shows up as a depression of the zero amplitude modulus by prior high-amplitude vibration, and also in the slow attainment of equilibrium by rubber under relatively high amplitude vibration, support the suggestion of a bond-breaking mechanism. The recovery of the shear modulus, n, after high amplitude vibration appears to follow no simple law, but a plot against log time shows only small curvature. It is not possible to measure n earlier than 30 seconds after the finish of the high-amplitude vibration and thus the instantaneous value of n at zero recovery time may only be estimated by a long extrapolation of the above curve to a time corresponding to the frequency. However, the figures involved are not inconsistent with the possibility that the zero recovery-time value of n is equal to the equilibrium high-amplitude modulus.

The fact that, with all the conventional fillers investigated, a unique pattern of modulus/amplitude characteristics is exhibited is a somewhat surprising result. Fillers differ in stiffening power, and different volume loadings of different fillers are required to give the same basic modulus value (n_0). Once this is fixed, the modulus-amplitude characteristic appears to be uniquely determined save for very minor differences. Within the amplitude limits here employed, all the fillers, when present in amount corresponding to a given degree of stiffening, confer upon the compound roughly the same distribution of structure-bond strengths.

Consideration of the measurements of loss factor show that the product $\omega\eta$ varies with amplitude to a much smaller extent than does modulus. In the course of a range of measurements from 0 to 3 per cent shear amplitude, no adjustment was made in the vibrating mass, and thus the modulus variation led to variation in test frequency. That such a change will not distort the $\omega\eta$ *vs.* amplitude characteristics is, however, clear. On the one hand, for highly loaded compounds, where the modulus and therefore the test frequency changes most with amplitude, it has been shown[2] that $\omega\eta$ is practically independent of frequency and, on the other hand, for gum stocks $\omega\eta$ is known to vary somewhat with frequency, but in such cases the modulus and, hence, the test frequency do not vary greatly with amplitude. All curves of $\omega\eta$ *vs.* amplitude given by pure-gum and loaded compounds show an early fall of $\omega\eta$ with increase of amplitude. It is noticeable that this fall is of about the same amount relative to the general level of $\omega\eta$ in all cases, and it seems unlikely, therefore, that the measured effect is due to any spurious feature coming from the apparatus. This phenomenon is interesting in that it is a feature of the simple gum compound as well as the reinforced stocks, and any explanation must take account of this fact.

At amplitudes beyond this initial range, all reinforced compounds show a small rise of $\omega\eta$ with increasing amplitude. This result is in agreement with

work by Dillon, Prettyman, and Hall[7], who made measurements of natural-rubber tread compounds at 50° C under conditions similar to those employed here. In contrast, Gui, Wilkinson, and Gehman[4], who carried out tests in compression, reported a continuous fall of their factor (analogous to $\omega\eta$) with amplitude over a similar range.

SUMMARY

Measurements are described of the dynamic properties of rubber, loaded with various amounts and types of filler, when subjected to mechanical vibration in simple shear at amplitudes from 0 to 3 per cent shear in the frequency range 20 to 120 c.p.s. The decrease of dynamic modulus with increasing amplitude is shown, for a wide range of filler types and concentrations, to be determined by the amount of stiffening produced by the filler. This relationship is not influenced by variations in the vulcanizing ingredients, reasonable variations in state of vulcanization, addition of softener, or imposition of static shear strain. Rubber compounds stiffened by mixture with, or chemical combination of, other polymers exhibit a smaller order of nonlinearity than that described above and also exhibit much lower hysteresis values within the amplitude range 0 to 3 per cent shear.

ACKNOWLEDGMENT

This work forms part of the research program undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] Dillon, Prettyman, and Hall, *J. Applied Physics* **15**, 309 (1944); Fletcher and Gent, *Trans. Inst. Rubber Ind.* **26**, 45 (1950); Waring, *Ind. Eng. Chem.* **43**, 352 (1951); Gui, Wilkinson, and Gehman, *Ind. Eng. Chem.* **44**, 720 (1952).
[2] Fletcher and Gent, *Trans. Inst. Rubber Ind.* **26**, 45 (1950).
[3] Waring, *Ind. Eng. Chem.* **43**, 352 (1951).
[4] Gui, Wilkinson, and Gehman, *Ind. Eng. Chem.* **44**, 720 (1952).
[5] Bloomfield, *Rubber Developments* **5**, 35 (1952); Blow, *Rubber Developments* **5**, 44 (1952).
[6] British Standards B.S. 903, Part 24.
[7] Dillon, Prettyman, and Hall, *J. Applied Physics* **15**, 309 (1944).

FACTORS AFFECTING THE MEASUREMENT OF STRAIN *

L. L. BEST

CHEMICAL DIVISION, RUBBER RESEARCH INSTITUTE OF MALAYA, KUALA LUMPUR, MALAYA

One of the most common physical tests of vulcanized rubber is the measurement of the stress-strain characteristics of a test-piece of uniform cross-section. The measurement is usually carried out on a tension testing machine, the test-piece being stretched between two clamps or pulleys which are separated at a constant rate. The stress and corresponding strain can be recorded autographically, and from the recording can be determined the stress required to produce a given elongation (modulus), the elongation at a given stress (strain), the elongation at break, and the final breaking tension stress. For a natural-rubber gum vulcanizate containing no fillers, the modulus is generally measured at 600 per cent elongation, since the stress at lower elongations is small and the percentage error arising in its estimate correspondingly large. It has been shown by Field[1] that, at elongations in excess of 200 per cent, vulcanized rubber contains an appreciable proportion of crystallized material, and the amount of crystallization depends on the temperature, state of vulcanization, and other factors. This effect, in combination with other uncontrolled variations, results in considerable disparities between the results of high-elongation modulus tests in different laboratories using similar test-pieces. It is, therefore, desirable that any accurate measurement of the stress-strain properties for the evaluation of natural or synthetic rubber should be made at elongations less than 200 per cent.

An apparatus was developed by U. S. National Bureau of Standards[2] which has the advantages of estimating the strain at elongations unaffected by crystallization both rapidly and accurately. The apparatus is designed so that the load on the test-specimen can be adjusted to apply a constant stress on the unstrained section of the test-piece over a practical range of cross-sectional areas. The application of the correct load is semiautomatic, but although the mechanism is relatively simple, its maintenance may be a problem in the producing countries in the East, especially on isolated stations. A modified but similar apparatus was designed by the British Rubber Producers' Research Association and has been described by Fletcher[3]; it has some advantages over the more elaborate model recommended by the Bureau of Standards, being inexpensive and easily maintained. There are, however, several minor disadvantages associated with the simpler strain tester which are mentioned below; nevertheless, the apparatus has proved to be an invaluable tool in the evaluation of the physical characteristics of natural rubbers.

The extensive employment of the strain test in the classification of natural rubber has resulted in a much more critical assessment of the strain test than is

* Reprinted from the *Journal of the Rubber Research Institute of Malaya*, Vol. 14, pages 149–162, September 1953.

usually given to new apparatus. This paper describes some of the work carried out in the R.R.I.M. in connection with this measurement.

GENERAL PROCEDURE EMPLOYED FOR PREPARATION OF COMPOUND, TESTING OF SPECIMENS, AND ANALYSIS OF RESULTS

All the experiments reported below were carried out using the A.C.S. No. 1 formulation, *i.e.*, smoked sheet 100, zinc oxide 6, sulfur 3.5, stearic acid 0.5, and mercaptobenzthiazole 0.5. The compounding ingredients were added in the form of masterbatches prepared with a small quantity of rubber, with medium modulus characteristics in the vulcanized state. This rubber, weighing 5 grams, forms a part of the 100 grams in the original formula. The mixing was carried out on a 6-inch diameter roll laboratory mill, with a time-controlled mixing procedure, so that the Mooney viscosity of the compound for each mix was 40 ± 3.

All test-pieces were vulcanized in a steam-heated hydraulic press for 40 minutes at 140° C. On removal from the molds, except as described later, they were cooled rapidly by immersion in water at laboratory temperature.

The testing temperature varied between 28° and 30° C; hence, none of the results may be immediately applicable to laboratories operating in temperate climates. However, limited results carried out by the French Rubber Institute, who were advised of the rapid test method in 1952, indicate that the correlation described in the section on Variation in Mixing, Vulcanizing, Testing Cycle may be independent of small temperature differences. Generally it should be noted that the temperature coefficient of strain measurements on test-pieces, prepared as described here, is of the order of $-0.2/°$ C. The strain measurement is made one minute after the application of a stress of 5 kg. per sq. cm., and is the increase of the elongation of a 10-cm. central length of a uniform section dumbbell.

The error in the measurement of strain is proportional to the mean value of the strain and strictly a logarithmic transformation should be employed prior to statistical analysis. Such transformations, however, do not appear to affect the significance of large effects and throughout this paper the simple although unorthodox procedure is employed.

PREPARATION OF TEST-PIECES

It has been found that the physical properties of a vulcanizate are affected by the periods between mixing and vulcanizing and between vulcanizing and testing. The variation for most physical properties is rapid in the first few hours after mixing and vulcanizing, but becomes small after about 24 hours. This effect has led most National Standards Institutions to advocate a period of storage of about 24 hours between both mixing and vulcanizing, and vulcanizing and testing. Thus, the time required to evaluate a sample of rubber is in excess of two days; in practice, the time interval is generally nearer three days due to the need to mix enough compound to use the complete capacity of the vulcanizing press. This delay has considerable disadvantages in the operation of a testing laboratory, whether it is employed in the producing countries or for check tests on industrial production. Although it was realized that any rapid test would not produce results similar to those obtained using a standard procedure, it was hoped that the results of the rapid and normal tests could be correlated and the correlation used for the determination of the latter from the former measurement.

VARIATION IN MIXING, VULCANIZING, TESTING CYCLE

Two samples of smoked sheet rubber of different technical properties in the vulcanized state were compounded in the A.C.S. No. 1 formulation and subsequently vulcanized in the form of strain dumbbells. The time cycle of the mixing, curing and testing procedures was varied as shown in Table I.

TABLE I

VARIATION IN STRAIN DUE TO DIFFERENT MIXING, CURING AND TESTING CYCLES

Time between mixing and curing in hours [T_2]	Modulus of rubber	Time between curing and testing in hours [T_1]			
		0	2	4	24
0	medium	82.6	81.3	79.6	81.5
	low	104.9	102.3	98.3	99.2
2	medium	82.7	80.7	81.5	80.6
	low	102.9	100.1	98.7	97.4
24	medium	81.3	79.2	78.3	78.4
	low	97.3	94.3	90.8	89.8

A statistical analysis of this data indicates that both the effects due to T_1 and T_2 are significant at the 5 per cent level. Consideration of the means of test-specimens produced under similar conditions shows that the two effects are of similar magnitude.

TABLE II

EFFECT OF CONDITIONING PERIOD ON PROPERTIES OF VULCANIZATE

T_1 in hours	0	2	4	24
Mean strain	92.0	90.0	87.9	87.8
T_2 in hours	0	2		24
Mean strain	91.2	90.5		86

This experiment suggests a rapid method for the measurement of strain. Provided that the time between the three major operations in the preparation and testing of the vulcanized specimens can be restricted to less than two hours, the results, although different from those attained by the normal methods, may be reproducible. The suggested procedure with a press vulcanizing 32 test-specimens at one loading is to mix this number of compounds (taking about 1½ hours) and test the vulcanizates immediately after immersion in cold water for about 10 minutes. The whole procedure takes less than 3 hours for this number of test-specimens.

CORRELATION BETWEEN RAPID AND NORMAL TEST

A large number of rubbers was examined, using the procedure outlined above, with the exception that the number of test-pieces vulcanized together varied between 3 and 12, corresponding to the intake of samples from a packing house. Subsequently tests were made by the normal procedure using the same compounded stock. In Figure 1 some of the strain results of the rapid test are recorded against the corresponding value obtained by the normal test method. The correlation coefficient of these results, uncorrected for variation in the cross-sectional area of the test-pieces, is 0.952 with 506 degrees of freedom. The equation of the best straight line drawn in Figure 1, for estimating the most

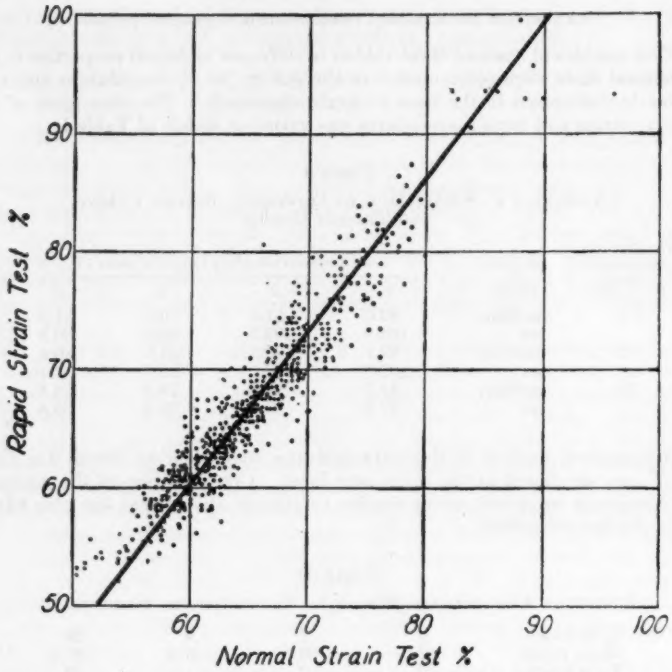


FIG. 1.—Correlation between strain results obtained by rapid and normal tests.

probable value of the normal result from measurements by the rapid test, is as follows:

$$S_N = 13.15 + 0.7746S_R$$

CONDITIONING OF COMPOUND AT MILL TEMPERATURE

It will be realized that the rapid method of test introduces considerable variations in the factors T_1 and T_2 if 32 test-specimens are examined at the same time. For example, the first compound will be conditioned at temperatures varying from about 70° (the mixing temperature) to 28° C (room temperature) for about 1½ hours, whereas the last compound will have had a very short period of conditioning at the higher temperature. It was found that if the compounds were maintained at 70° C for up to 2 hours, the change in strain of the vulcanized test-piece was not significant in comparison with the experimental error, which suggests that the compound should be retained at 70° C after removal from the mixing mill until all mixing had been completed. In this manner, although the different compounds may be conditioned for varying times at 70° C, their physical properties should not be altered significantly. The following experiment was carried out to determine whether the retention of the compound at the mill temperature would improve the reproducibility of the rapid test.

Pieces from 29 blended bale samples of ribbed smoked sheet were compounded in the A.C.S. No. 1 formulation. Each compound was divided into three parts and treated as follows:

(1) A 5-gram blank was cut from the compound immediately after sheeting and placed in an oven at 70° C. When all the compounds were mixed, the 22 blanks were placed in two strain molds and vulcanized for 40 minutes at 140° C (S_1).
(2) When all the compounds were prepared, blanks were cut from each compound and placed in the molds and vulcanized as before (S_2).
(3) One day after mixing, a 5-gram blank was cut from each compound, vulcanized as in (1), and tested on the following day (S_3, normal test).

All test-pieces were cooled in water at about 28° C immediately after removal from the molds. The test-pieces obtained from treatments (1) and (2) were tested between ½ and 1¾ hours after vulcanization.

Figure 2 gives the results of the two rapid tests recorded against the corresponding values of the normal test. The best straight lines for predicting values of the normal strain test from those of the rapid text are drawn for both relations. The correlation coefficients of the rapid tests with the normal test S_1/S_3 and S_2/S_3 are 0.98 and 0.99, respectively, there is considerably less probability than 1 in 1000 of such values occurring by pure chance. The two lines are significantly different with respect to both slope and axis interceptions.

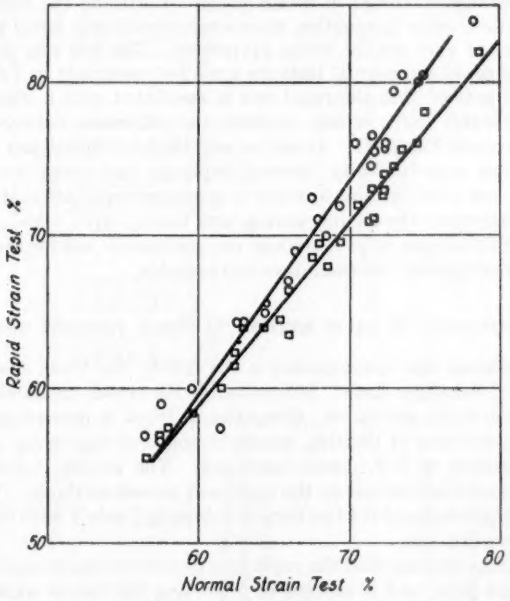


FIG. 2.—Comparison of the rapid test with and without controlled conditioning of compound.

□ Free cooling of compound for rapid test.
○ Compound conditioning at 70° C for rapid test.

An examination of the residual variance about the regression line indicates that there is less variability associated with the free cooling rapid test than with that conditioning the compound at the mill temperature. Comparison of these data with those given in Figure 1 suggests that all the data can be regarded as being of the same population.

MIXING, CURING, AND TESTING ERRORS WITH THE NORMAL AND RAPID TEST METHODS

Since, with the rapid method, the rubber would be exposed for short periods to uncontrolled variations, it was expected that the total error associated with the mixing, curing, and testing would be less than with the normal method. The effects of all three operations on the two methods of test are compared in the experiment described hereunder.

Eight blended samples were selected; six ribbed smoked sheet and two thin pale crepe, giving a fairly wide range of physical properties in the vulcanized state. One mix was made from each rubber on each of three days; four strain test-pieces were vulcanized from each mix, two by the rapid method and two by the normal procedure. The mixings were carried out in a random order within days.

The results of the measurements corrected for cross-sectional area variations are given in Table III. An analysis of these results (not reported) shows that there is a significant interaction between samples and method of test. This tendency to change the order of strain values by altering the method of test will cause little trouble in practice, since confusion is only likely to occur between rubbers of very similar strain properties. The two sets of results obtained by the rapid and normal tests are analyzed separately in Table IV.

It will be noticed that the rapid test is associated with a slightly greater between duplicates error, which confirms the difference between duplicate test-pieces given in Table III. It will be seen that, on days 1 and 2, the rapid test has similar reproducibility between duplicate test-pieces, to that of the normal test, but that, on day 3, there is a greater error associated with the rapid test. However the mixing, curing, and testing error, which can be estimated from the between days' variance, is considerably less for the rapid test, as is also the interaction between days and samples.

APPLICATION OF RAPID METHOD TO OTHER PHYSICAL TESTS

Sixteen rubbers were compounded in the A.C.S. No. 1 mix and vulcanized in the form of Schopper discs. Subsequently the strain, modulus at 660 per cent elongation in kg. per sq. cm., elongation at break in percentage of original internal circumference of the ring, tensile strength of ring in kg. per sq. cm., and B.S. hardness in B.S.°, were measured. The mixing, vulcanizing and testing cycles were carried out by the rapid and normal methods. The correlation between the results of the two tests are given in Table V with the equations of the best straight line.

These results indicate that the rapid test procedure can be used for a number of physical tests, and is capable of predicting the values which would be obtained by normal standard procedures. As expected the relation between the two methods when measuring tensile strength is associated with the most

TABLE III

RESULTS OF RAPID AND NORMAL TESTS CORRECTED FOR CROSS-SECTIONAL AREA ERRORS

	Strain [40 minutes at 140° C]					
	Day 1		Day 2		Day 3	
Sample	Rapid	Normal	Rapid	Normal	Rapid	Normal
1	62.5, 62.5	60.0, 59.5	62.0, 62.5	60.5, 60.0	63.0, 62.0	59.5, 60.0
2	60.0, 59.0	59.5, 58.5	59.5, 58.5	54.5, 55.0	59.5, 58.5	57.0, 57.5
3	84.0, 83.5	77.5, 77.0	80.5, 82.5	77.5, 78.5	83.0, 80.0	79.5, 78.0
4	75.0, 75.5	74.5, 75.0	75.0, 74.0	72.5, 72.0	73.0, 74.5	71.5, 72.0
5	93.5, 93.0	90.0, 89.5	92.0, 92.0	84.5, 86.0	93.0, 93.0	86.0, 85.5
6	85.0, 83.0	82.5, 80.0	84.0, 84.5	79.0, 80.5	82.5, 82.0	78.5, 77.5
7	111.5, 110.0	99.5, 100.0	112.0, 114.0	101.5, 100.5	114.0, 110.5	98.0, 98.5
8	111.0, 113.5	102.0, 103.5	113.0, 113.0	97.5, 98.5	109.5, 112.0	99.0, 97.5
Total difference between duplicate test-pieces	8.5	7.5	7.0	7.5	13	6.5

TABLE IV

COMPARISON OF ANALYSIS FOR RAPID AND NORMAL TESTS

		Rapid test			Normal test		
Source of variation	d.f.	S.S.	M.S.S.	Probability	S.S.	M.S.S.	Probability
Between samples	7	16891.4531	2413.0647	<0.001	10824.4167	1546.3452	<0.001
Between days	2	5.1982	2.5991	<0.02	40.3229	20.1614	0.05
S × D	14	21.2188	1.5156	>0.02	76.6771	5.4769	<0.001
Between duplicate test-pieces	24	28.3750	1.1823		13.5000	0.5625	
Total	47	16946.2451			10954.9167		

TABLE V

CORRELATION BETWEEN RAPID AND NORMAL PROCEDURES FOR DIFFERENT PHYSICAL TESTS

Test	Correlation coefficient	d.f.	Probability	Equation of regression line
Modulus	0.978	14	<.001	$M_N = 4.85 + 0.9783\ M_R$
Elongation at break	0.977	14	<.001	$E_N = 125.3 + 0.8512\ E_R$
Tensile strength	0.926	14	<.001	$T_N = 16.77 + 0.9396\ T_R$
Hardness	0.998	14	<.001	$H_N = 1.43 + 0.9756\ H_R$

scatter about the regression line, although the correlation coefficient is still highly significant.

COLD WATER IMMERSION OF TEST-PIECE AFTER VULCANIZATION

Most national standards recommend that the test-pieces should be immersed in cold water for ten minutes after removal from the vulcanizing molds. One hundred and ninety-two compounds were prepared, and two strain specimens vulcanized from each; one test-specimen was allowed to cool to room temperature without any special control; the other was immersed in water at room temperature after removal from the mold. The mean values for the chilled and unchilled specimens were 81.35 and 81.40, respectively, indicating that little difference in low elongation strain measurements is introduced by the rapid cooling of the test-pieces.

THE VARIATION OF STRAIN MEASUREMENTS DUE TO ERRORS IN THE CROSS-SECTIONAL AREA OF THE TEST-SPECIMEN

Operating under laboratory conditions, it would be possible with the strain molds employed with the British Rubber Producers' Research Association strain tester to avoid the larger fluctuations in the cross-sectional area of the test-pieces by the selection of test-pieces. In practice, however, a testing station working with a large input of samples can in general only vulcanize one or two test-specimens of each sample, and the problem of correction for variation in cross-sectional area becomes acute. The most satisfactory solution to this problem would be the design of an improved mold, and work is in progress with this end in view. Temporarily a system of correction has been introduced in Malaya, based on the following theory.

For small variations in strain, it has been shown experimentally that ds/da = constant $= -K_s$, where s is the measured strain value, corresponding to a test-specimen section of a sq. cm.

The values of K_s for different values of strain can be calculated, indicating a relation of the form $K = bS + c$, where S is the true strain value corresponding to a section of 20 sq. mm. Then

$$ds/da = -K = -(bS + c)$$
$$s = -bSa - ca + R$$

where R is a constant with respect to a. But

$$S = s + \delta s = -bS\,(a + \delta a) - c\,(a + \delta a) + R$$
$$\therefore S - s = -bS\,\delta a - c\,\delta a$$
$$S = (s - c\,\delta a)/(1 + b\,\delta a) \qquad [1]$$

When ds/da is small, S approaches $-c/b$ and then

$$s = -c/b \qquad [2]$$

Blackwell[4] has proposed a similar equation to [1] which is based on the assumption that stress-strain curves can be represented to a first approximation by a relationship of the form:

$$S = aF^2 + bF$$

where S and F are the strain and stress, respectively, and a and b are constants independent of the physical characteristics of the rubber.

Nine samples of smoked sheet of different physical characteristics in the vulcanized state were compounded in the A.C.S. No. 1 formulation, and sixteen test-pieces vulcanized from each compound in the same mold. The strain value of each test-piece was measured, and the corresponding value of the cross-sectional area of the central test-length. The cross-sectional area was determined by cutting approximately 7 cm. from the central portion of the dumbbell, using a parallel bladed cutter and a Schopper ring cutting press. The standard deviation in the cut length for 12 test-specimens, measured by a comparator, was ± 0.14 mm. and the concavity of the end sections was almost imperceptible when the knife edges were sharp and the cut made rapidly. From the mass of the central length and the specific gravity of the rubber, the area of the section of the test-pieces was calculated.

In order to determine which dimension was primarily associated with the variation in cross-sectional area, measurements were made with a dial-gauge micrometer, fitted with a flat foot. This method usually gives too small an assessment of the section, presumably due to the compression of the test-piece under load; the average reduction in section is of the order of 1 per cent. Nevertheless, the measurements indicate that the variation of area is mainly associated with the width of the test-piece rather than the thickness, suggesting that the mold cavities are being distorted laterally during service.

The correlation coefficient, with fourteen degrees of freedom, between the strain and the cross-sectional area measurements for the nine compounds are given in Table VI with the corresponding values of S and K.

The equation of the best straight line for deriving values of K from S is:

$$K = 4.836 - 0.154\,S$$

thus giving the appropriate values of the constants a and b in Equation [1].

Using Equation [1] and the values of the constants determined, a series of lines were constructed, relating the measured and true strain for different errors in the cross-sectional area of the dumbbell. The correction curves are given in Figure 3; it will be noticed that the error is small for vulcanizates with low strain or high moduli, the correction approaching zero when the strain is of the order of 31 units. At higher strain values, the correction is large; at

TABLE VI

CORRELATION BETWEEN STRAIN AND SECTION OF TEST-PIECE

Compound	1	2	3	4	5	6	7	8	9
Correlation coefficient	−0.80	−0.84	−0.82	−0.86	−0.78	−0.76	−0.89	−0.90	−0.74
Strain [S]	66.7	89.5	67.3	82.2	60.0	99.8	100.5	61.0	87.3
K	−6.50	−11.57	−4.38	−6.60	−3.98	−12.30	−9.08	−5.62	−6.81

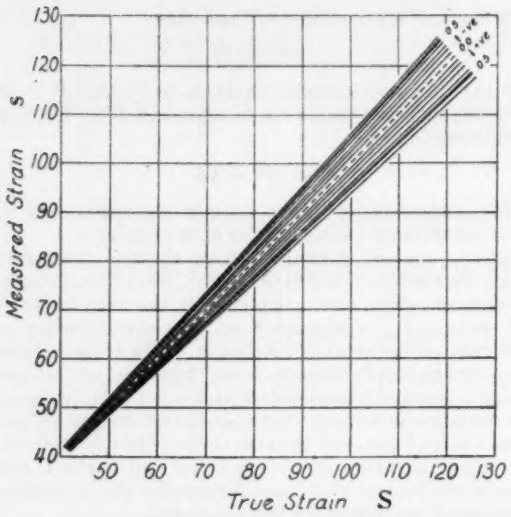


FIG. 3.—Correction curves for cross-sectional area variations from +0.6 to −0.6 sq. mm.

$S = 110$ it is of the order of $\pm$ 7 units for $\pm$ 0.6 sq. mm. error in the area of the section.

A more convenient method of correcting for cross-sectional area variations in strain measurements is to obtain a similar series of curves for the mass of a fixed length of test-piece; a mean value of the specific gravity of the A.C.S. No. 1 compound should then be used. The variations for different samples of smoked sheet rubber are comparatively small and the errors introduced by this assumption small, of the order of 0.4 per cent. The procedure then becomes: measure the strain, cut the central test-length from the specimen, and weigh it,

TABLE VII

CORRECTION OF STRAIN FOR CROSS-SECTIONAL AREA OF TEST-PIECE

Rubber	C.S.A. sq. mm.	Measured strain	Corrected strain
High strain	19.93	105.0	104.0
	19.50	108.0	103.0
	19.86	106.5	105.0
	20.09	98.5	99.5
	20.52	93.5	98.5
Medium strain	19.88	82.0	81.0
	20.36	81.0	84.0
	19.72	86.0	83.5
	20.19	81.0	82.5
	20.46	78.5	82.0
Low strain	20.44	58.5	60.5
	20.42	58.5	60.5
	20.16	59.5	60.5
	19.55	61.0	59.5
	20.18	60.0	61.0

find the true strain for a test-piece of this section and measured strain from the curves.

Application of the Correction.—Five test-specimens were prepared from each of three rubbers of different intrinsic physical properties. The strain and cross-sectional area of each test-specimen was measured, and the corrected strain value was determined. The results are given below in Table VII.

A statistical analysis of these data shows that the correction reduces the standard deviation of the measurement from $\pm$ 3.9 to $\pm$ 1.8 units of strain.

CONCLUSIONS

1. Although alteration of the mixing, vulcanizing, and testing cycle for the measurement of strain does affect the physical properties of the final vulcanizate, a high degree of correlation can be obtained between the results of the rapid test and the normal test. The rapid test, which will not consume any more man-hours than the normal test, can be fitted in to the normal daily procedure with little loss of testing capacity, and provides satisfactory data in a period of three hours for thirty-two test-specimens, whereas more than two days are needed by the normal standard procedure.

2. The mixing, curing, and testing error associated with the measurement by the rapid method is less than that obtained with the normal test method.

3. The rapid method can be used for predicting the results which would be obtained by many physical tests carried out by standard procedures and would, therefore, be generally useful for control measurements in industrial concerns.

4. Isothermal conditioning of the compounded stock after mixing does not appear to reduce the error associated with the rapid test, but does alter the relation between the rapid and normal tests.

5. Immersion of test-specimens in cold water after vulcanization does not improve reproducibility or alter the value of the strain measurement.

6. Molded strain specimens are liable to vary in respect of cross-sectional area. Such variations can produce considerable errors in strain measurements, particularly with rubbers of high strain or low modulus characteristics. A simple method for the correction of these errors is advanced which increases the reproducibility of the strain test.

REFERENCES

[1] Field, *J. Applied Physics* 12, 23 (1941); RUBBER CHEM. & TECHNOL. 14, 555 (1941).
[2] Schade and Roth, "Symposium on Rubber Testing", ASTM Special Techn. Publ. No. 74, p. 27 (1947).
[3] Fletcher, RUBBER CHEM. & TECHNOL. 23, 107 (1950).
[4] Blackwell, Variability of Rubber Report No. 27, (1950) of the British Rubber Producers' Research Association, not yet published.

THE VELOCITY AND TEMPERATURE DEPENDENCE OF RUBBER FRICTION *

A. SCHALLAMACH

THE BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION,
WELWYN GARDEN CITY, HERTFORDSHIRE, ENGLAND

INTRODUCTION

The coefficient of dynamic rubber friction has received little attention in the literature. Qualitative experiments by Ariano[1] and Derieux[2] showed that the coefficient of rubber friction increases with increasing sliding velocity, and this was confirmed by Roth, Driscoll and Holt[3]. These authors experimented with rubbers of the tire tread type, and found that the friction of such samples on plate glass increases slowly with increasing velocity, the rate of increase being lower than would be given by a logarithmic velocity dependence.

The published data on the temperature dependence of rubber friction are even scantier and appear to be the result of *ad hoc* experiments made in connection with specific technological problems. Breuil's experiments[4] were inconclusive, and Ariano[1] found that the coefficient of rubber friction falls with increasing temperature.

We have investigated both velocity and temperature dependence of rubber friction by a method based on the fact that the positive velocity coefficient of rubber friction makes it possible to cause rubber to slide over a track at a constant velocity by application of a sufficiently high constant tangential stress. As mentioned above, the velocity coefficient is low so that relatively small variations of the tangential stress produce large changes of the sliding velocity, and a wide range of velocities can be covered in this way without the necessity of elaborate gear boxes or similar devices. Further advantages of this method of studying rubber friction will become apparent later. This paper reports the results of measurements of the sliding velocity at various tangential stresses and temperatures.

EXPERIMENTAL

The apparatus used for our experiments was a modified form of that described in an earlier publication[5], to which reference is made for details of the shape of the samples. The geometrical contact area of the samples was in the present case 5.4 sq. cm.

In order to control the temperature, the horizontal track was made hollow and water was pumped through it from a thermostat. The track was housed in a box lined with copper tubing, which was connected in series with the hollow of the track so that an approximately uniform temperature was maintained within the enclosure. The temperature difference across the thickness of the sample did not exceed 0.25° C.

* Reprinted from the *Proceedings of the Physical Society* (London), Series B, Vol. 66, pages 386–392 (1953).

The constant tangential stress was provided by lines which passed over free pulleys and carried hanging weights. The sliding velocity was automatically recorded by trailing behind the sample a paper strip on which a simple timing mechanism made marks at given intervals.

Preliminary experiments had shown that, because of the sensitivity of the method, special precautions had to be taken in order to obtain reproducible results. The first requirement was to reproduce the surface of the track as nearly as possible, and it was found that using ground plate-glass and regrinding it after each run gave the most reliable results. The abrasive used for this purpose was carborundum, (Grade 1F). Additional measurements were made on silicon-carbide cloth (John Bull No. 150); by using fresh abrasive for each run reproducible results were obtained on this type of track.

In order to remove from the samples substances which might ooze out during the course of the experiment and produce random self-lubrication, the samples were extracted for 48 hours with alcohol-toluene azeotrope[6], followed by 24 hours' extraction with alcohol, and subsequent vacuum-drying. An unfortunate consequence of extraction of most types of rubber compound is that both natural and added antioxidants are removed thereby, and noticeable oxidation sets in within a matter of days. As it was not always possible to finish an investigation within this time, more than one sample had sometimes to be employed in the course of one investigation. All experiments were carried out with an unloaded vulcanizate of natural rubber of the following composition: rubber 100, zinc oxide 5, sulfur 2.5, Santocure (accelerator) 0.6, phenyl-β-naphthylamine (antioxidant) 1.0, stearic acid 1.0. The samples were cured for 50 minutes at a temperature of 142° C.

RESULTS

MEASUREMENTS ON GROUND GLASS

In our measurements, the normal load on the sample was always 6.44 kg. In view of the fact that the true tangential stresses depend on the actual area of contact between rubber and track[5], the absolute value of which is not known, the results are given in terms of the pulling weights which actuated the samples.

When rubber slides on a surface which produces little abrasion, the sliding velocity decreases rapidly as the sample travels along the track. This is demonstrated for two different pulling weights of, respectively, 5.8 and 7.8 kg. in Figure 1. In the case of curve *a*, there is no indication of the velocity becoming constant, and eventually the sample did indeed stop. In case *b*, however, the sliding velocity became constant after a travel of about 10 cm. It is obvious that the pulling weight of 5.8 kg. corresponds to less than the ultimate value of the coefficient of static friction, and it will be seen that an accurate determination of this quantity would be a matter of some complexity. Under the conditions obtaining in our experiments, 7.8 kg. was found to be near the limiting pulling weight which would produce steady motion.

When the pulling weight is increased in the course of the measurement, the final value is attained very much sooner than when the measurements are begun with a new sample, and it appears that, during sliding, a conditioning of the surface is brought about. If the pulling weight is momentarily removed, the conditioning is partly lost. If, at the same time, the sample is lifted off the track, the conditioning virtually disappears. The practical importance of this effect is that much time is lost in reconditioning the sample after it has traversed

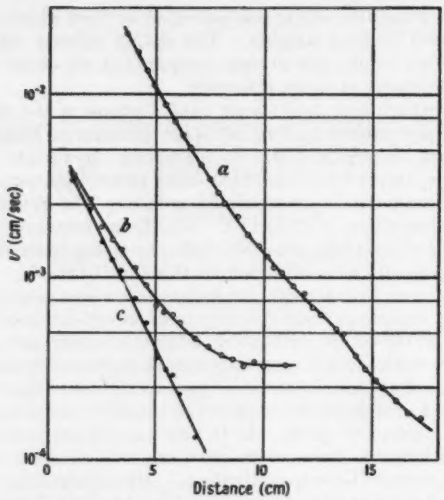


FIG. 1.—Sliding velocity on ground glass plotted against distance travelled. Pulling weight: *a*, 5.8 kg., *b*, 7.8 kg. Curve *c*: curve *b* replotted as log [(*v* − 0.00036) cm/s] against distance travelled.

the whole length of the track and a new run is started. In view of the need for haste caused by the degradation of the samples by oxidation, a small alteration was made in the experimental arrangement. The track was divided into two equal sections in tandem, *i.e.*, one section in front of the other, the butt joints being accurately ground square so as to present only a small discontinuity to the sample when travelling over it. After the sample had cleared the first section, this was removed for regrinding; then the second section, with the sample on it, was pulled back and the first section inserted in front of it. This procedure made it possible to conduct the experiment without ever lifting the sample off the track, and to determine reproducible curves with one and the same sample.

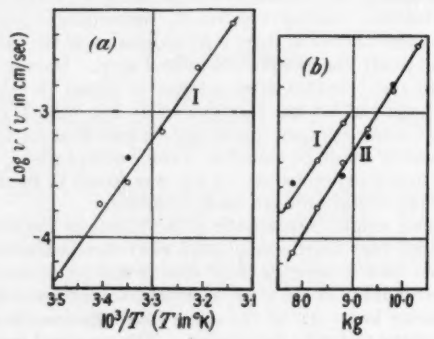


FIG. 2.—Steady state sliding velocity on ground glass as a function of (*a*) the reciprocal absolute temperature for sample I with a pulling weight of 7.7 kg., (*b*) the pulling weight for samples I and II at 25° C.

The results showing the steady state velocities obtained with two samples are shown in Figure 2. The full circles in both graphs are repeat points. The curve of Figure 2(*a*) is, within the limits of experimental error, a straight line; similarly, the graphs of Figure 2(*b*) are very nearly linear apart from the region of the lowest pulling weights in the neighborhood of the values corresponding to the static coefficient of friction.

Curves I and II in Figure 2(*b*) illustrate the divergent absolute values of the sliding velocities which may be obtained with nominally similar samples; the slopes of the curves, on the other hand, appear to be very similar. The range of pulling weights within which steady sliding is possible had an upper limit of about 10 kg. If this limit was exceeded the sample accelerated slowly.

Figure 2 shows that in the first approximation the sliding velocity of rubber on ground glass is (1) an exponential function of the reciprocal absolute temperature, (2) an exponential function of the pulling weight as long as this is sufficiently large compared with the weight necessary to overcome static friction. During the measurements, a certain amount of abrasion occurred and it was observed that mold marks on the surface of the sample were worn away; also, the sample left a faint trace on the track. The magnitude of the abrasion was, however, too small to be determined by weighing.

MEASUREMENTS ON SILICON–CARBIDE CLOTH

Frictional sliding of rubber on silicon-carbide cloth depends far less critically on the experimental conditions than was found in the case of ground-glass tracks. In particular, there is no conditioning of the surface, and the sample

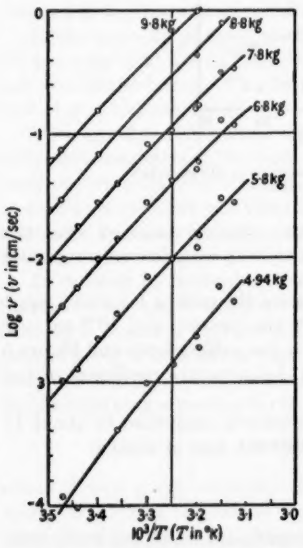


FIG. 3.—Steady state sliding velocity on silicon-carbide cloth plotted against reciprocal absolute temperature for various pulling weights.

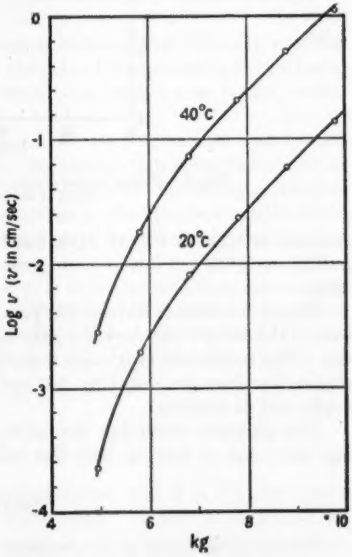


FIG. 4.—Steady-state sliding velocity on silicon-carbide cloth plotted against pulling weight.

slides at constant velocity almost immediately after it has been started. Also, steady running is possible in a wider region of pulling weights and velocities, this extension of the working range being mainly due to a lower static coefficient of friction. It might be pointed out here that the coefficient of friction is lower on the coarser surface of the abrasive than on the smooth surface of the ground glass because the local normal pressure where the rubber is indented by the particles of the abrasive is high[5].

Figure 3 shows the results of the measurements of the sliding velocity on silicon-carbide cloth. The graphs have a slight curvature and can again in the first approximation be considered as linear. Figure 4 gives the logarithm of the sliding velocity at two constant temperatures as a function of the pulling weight, the points on this graph having been interpolated from Figure 3. This

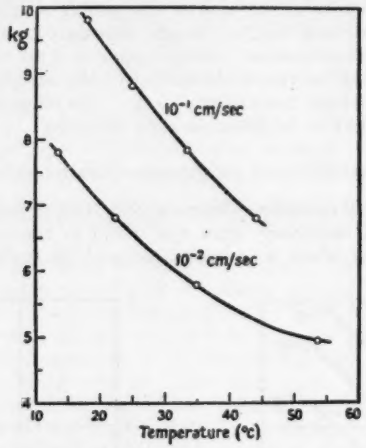


FIG. 5.—Pulling weight plotted against temperature on silicon-carbide cloth at two constant velocities.

graph is similar to Figure 2(*b*), but the fall of the sliding velocities when the pulling weights are low is more pronounced than was experienced on ground glass.

Figure 5 is also derived from Figure 3 and gives the pulling force as a function of the temperature at the velocities of 10^{-1} cm. per sec. and 10^{-2} cm. per sec. The coefficient of friction is proportional to the pulling force and Figure 5 shows therefore the negative, but not constant, temperature coefficient of the coefficient of friction.

The abrasion occurring during these measurements amounted to about 17 mg. for a run of 100 cm. and was independent of the rate of sliding.

DISCUSSION

The decrease of the sliding velocity of rubber on tracks which have only little abrasive effect (Figure 1) has its counterpart in the initial rise of the frictional force which is observed when friction measurements are made at constant

velocity[3]. It has been suggested above that this effect is due to a conditioning of the rubber surface; its absence on an abrasive track where the surface is constantly renewed lends weight to this assumption. The effect arises most probably from an increase of the true area of contact between rubber and track under the combined influence of normal load, tangential stress, and sliding. An increase of the true area of contact would lead to an enhanced frictional force as has been shown elsewhere[5]. A similar phenomenon in metallic friction has been demonstrated by McFarlane and Tabor[7].

It may be observed that curve *b* of Figure 1 can be described by the simple mathematical relation: $v_x - v = \text{const. exp. } (-x/l)$, where v is the final velocity, x is the distance travelled and l is a constant; this is shown by the linearity of curve *c* of Figure 1.

The most interesting feature of the results is, perhaps, the temperature dependence of the sliding velocity at constant pulling force F which can be approximately described by the equation:

$$v_{F=\text{const}} = A' \exp. (-E'/\mathbf{k}T) \tag{1}$$

where A' and E' are constants. Equations of this type are familiar in connection with physical rate processes, such as viscous flow. Whenever an experimental result is adequately described by an equation of this kind, the process in question is generally assumed to be actuated by an activation mechanism, that is to say, it is assumed that the elementary particle taking part in the process is confined to a potential trough from which it escapes from time to time into neighboring troughs because of thermal collisions, and that under the influence of an external stress these jumps occur no longer completely at random, but are directed in such a way as to relieve the stress.

In the majority of cases, the applied stress is so small that it hardly modifies the potential field within the material, and the rate of the process is then a linear function of the stress. The best known example of such a case is the viscous flow of a newtonian liquid.

We suggest that the frictional sliding of rubber is a rate process based on an activation mechanism, the main reason for this assumption being the observed temperature dependence of frictional sliding. Without discussing a detailed molecular model, one can visualize the conditions in the interface rubber-track as similar to those between two adjacent layers of molecules in the laminar flow of a viscous liquid of high molecular weight.

In contrast to newtonian flow, the velocity is in the present case not a linear function of the applied stress, and this is thought to be because the intermolecular field is modified by the relatively large tangential stress. Where the tangential stress is sufficiently high compared with the value corresponding to the static coefficient of friction the experimental results can, in fact, be expressed by the following equation for v:

$$v = A \exp - (E - \gamma F)/\mathbf{k}T \tag{2}$$

where A and γ are constants, F is the pulling force, and E is the activation energy measuring the height of the potential trough. It will be seen that, on the basis of Equation (2), the activation energy is not proportional to the slope of the curves of Figures 2(*a*) and 3, which depends also on the tangential stress. By carrying out partial differentiation of Equation (2) with respect to $1/T$ and

F, the slope of the log $v = f(1/T)$ curves is obtained as:

$$[\partial \ln v/\partial(1/T)]_F = -E/\mathbf{k} + FT(\partial \ln v/\partial F)_T. \quad (3)$$

The second term on the right-hand side of Equation (3) should effect a decrease of the slope with increasing tangential stress. The accuracy of our experiment was not great enough definitely to confirm this prediction. The values of E calculated by means of Equation (3) are given in the following table, $[\partial \ln v/\partial(1/T)]_F$ having been obtained from Figures (2*a*) and 3, and $(\partial \ln v/\partial F)_T$ from Figures 2(*b*) and 4.

	Rubber on ground glass	Rubber on silicon carbide
Pulling weight (kg.)	7.7	7.8
$-\mathbf{R}\,[\partial \ln v/\partial(1/T)]$ (cal. per mole)	26,600	20,400
E (cal. per mole)	19,880	16,160

The order of magnitude of the activation energies for frictional sliding given in the table is the same as that found for other activation processes in vulcanized natural rubber; for example, the activation energy for dielectric relaxation[8] is 17 kcal. per mole. It is interesting to note that Eyring's theory[9] of non-newtonian flow leads, for large tangential stresses, to an expression for the rate of flow which is formally identical with Equation (2).

The explanation of our experimental results, as set out above, takes no cognizance of abrasion and, in fact, divorces abrasion completely from friction, in contrast to current theories of solid friction. We are not yet in the position to state definitely that frictional sliding of rubber can take place without any abrasion occurring, although experiments with rubber on plate glass appear to suggest this possibility.

Another query arising out of our measurements on silicon-carbide cloth is what part of the frictional force is due to abrasion, and what part to friction proper, and how far the results are determined by the ratio of these two contributions. As the rate of abrasion is independent of the velocity, it is safe to say that the fraction of the tangential stress necessary to balance the abrasive effort is constant in the whole range of velocities employed by us, and that the corresponding correction of the graphs of Figure 4 consists of an horizontal displacement of the origin towards the right. The main points of our argument are not affected by this adjustment.

The absolute value of the contribution of abrasion to the measured frictional force is more difficult to estimate, but a lower limit of this quantity can be given without difficulty. Assuming that each particle of the debris has been removed from the bulk rubber in one single action, the total energy necessary to produce the debris can be calculated from the known energy density at break of the rubber. It is found in this way that the force necessary to produce the debris at the observed rate is 0.15 kg. It will be seen that, say, ten times this figure would still lead to a relatively small contribution to the total frictional force.

SUMMARY

It is shown experimentally that the velocity of frictional gliding under constant tangential stress of rubber on glass and on silicon carbide cloth is, in the first approximation, an exponential function of the reciprocal absolute temperature and of the tangential stress. It is suggested that frictional gliding of rubber is a rate process.

ACKNOWLEDGMENT

This work forms part of the research program undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] Ariano, *Politecnico* **10**, 11 (1930); RUBBER CHEM. & TECHNOL. **3**, 287 (1930).
[2] Derieux, *Elisha Mitchell Sci. Soc.* **50**, 53 (1934); RUBBER CHEM. & TECHNOL. **8**, 441 (1935).
[3] Roth, Driscoll, and Holt, *J. Research Natl. Bur. Standards* **28**, 439 (1942).
[4] Breuil, *Caoutchouc & gutta-percha* **7**, 4257 (1910).
[5] Schallamach, *Proc. Phys. Soc.* (London) **B65**, 657 (1952).
[6] Griffith, Story, Barkley, and McGilvray, *Anal. Chem.* **20**, 837 (1948).
[7] McFarlane and Tabor, *Proc. Roy. Soc.* (London) **A202**, 244 (1950).
[8] Schallamach and Thirion, *Trans. Faraday Soc.* **45**, 605 (1949).
[9] Eyring, *J. Chem. Physics* **4**, 283 (1936).

NOTES ON THE USE OF PLASTICITY TESTS TO ASSESS SCORCHING OF RUBBER STOCKS *

R. W. WHORLOW

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

INTRODUCTION

Two methods are in common use for determining the rate of scorching of a rubber mix, that is, the period at processing temperatures before the first stages of vulcanization appreciably stiffen the mix. The first method uses a Williams or other compression plastometer; test cylinders are prepared, heated for suitable periods at a temperature at which scorching will occur, and subsequently tested in the plastometer at some lower temperature at which scorching is negligible in the period of test. In the second method, a rotation instrument such as the Mooney viscometer is used; a test-piece is loaded into the instrument, and after one minute's preheating the motor is started and is run until an increase in the torque required to shear the rubber indicates scorching.

In this report no attempt is made to give criteria by which the behavior of stocks during actual processing could be judged from scorch test results, but three aspects of the method of test are considered. First, some results are given on the influence of compression plastometer design and operation on sensitivity in detecting scorching; second, the influence of the method of preheating test pieces prior to compression tests is studied; and finally, scorch rates determined by compression and rotation methods are compared.

It should be pointed out that compression tests are here used only for stocks not containing reinforcing carbon blacks. It has been shown elsewhere[1] that misleading results will frequently be obtained on stocks loaded with reinforcing carbon blacks, for which only rotation type (*e.g.* Mooney) tests and possibly extrusion tests, are reliable.

COMPRESSION PLASTOMETERS: METHODS OF TEST

In order to determine the test conditions most sensitive to scorching, experiments were carried out on test-pieces, either unheated or heated 105 minutes at 100° C and rapidly cooled, of the following mix (Mix A): smoked sheet 100, stearic acid 1, zinc oxide 5, butyraldehydeaniline 0.5, and sulfur 2. Two instruments were used, covering widely differing conditions of test: (1) the standard Williams plastometer (5-kg. load on parallel-plane surfaces) at 70° C, readings of compressed thickness in mm./100 units being obtained after ¼, ½, 1 and 5 minutes' compression, and (2) a modified Defo plastometer used as a constant-load instrument. This latter instrument compresses test-pieces between 1-cm. diameter anvils, and was used with two loads (300 and 625 grams), and at two temperatures (70° C and 90° C) with readings at ¼, ½, 1 and 2 minutes. Test-pieces, which were 1-cc. cylinders 11 mm. in diameter for

* Reprinted from the *India-Rubber Journal*, Vol. 125, No. 6, pages 214–217, August 8, 1953.

Williams tests, and the standard 1 cm. diameter by 1-cm. long cylinders for Defo tests, were preheated for 15 minutes at the test temperature immediately before test. Recovery was measured in all cases; after five minutes' compression and eight minutes' recovery at room temperature for Williams tests, and after two minutes' compression and either ¼ or two minutes' recovery at the test temperature in the Defo tests.

In all cases, five tests were made on both unheated and heated cylinders, and an analysis of variance was carried out on these ten results. In order to obtain a measure of the efficiency of the tests in detecting scorching, the discriminating power (defined as the ratio of the variance "between heating periods" to the variance "within heating periods") was calculated for each test. All discriminating powers are quoted relative to the value for the Williams five minutes' compression test, taken as unity. The procedure follows that adopted previously[2] in comparing the efficiency of various methods in detecting differences in mastication of rubbers, but in the present case it is not strictly valid as the variability of repeat results on scorched test-pieces is considerably greater

TABLE 1

RELATIVE DISCRIMINATING POWERS OF WILLIAMS AND MODIFIED DEFO TESTS IN DETECTING SCORCHING

Compression period (min.)	Mean test-piece thickness (mm./100)				Relative discriminating power	
	Williams		Defo			
	Unheated	Scorched	Unheated	Scorched	Williams	Defo
¼	271	287	690	718	0.05	0.08
½	243	259	588	637	0.09	0.25
1	214	235	481	549	0.25	0.48
2	—	—	380	457	—	0.75
5	161	184	—	—	1.0	—
Recovery period (min.)						
¼	—	—	437	560	—	0.98(0.84)
2	—	—	508	691	—	1.3(1.8)
8	191	228	—	—	5.0(1.6)	—

than on unheated test-pieces, and, therefore, exact statistical tests cannot be applied. However, the relative discriminating power provides a convenient approximately quantitative measure of the efficiency of the tests. Table 1 gives the mean values of compressed thickness and recovered thickness and the relative discriminating powers for the Williams test and the Defo 70° C, 300-gram test.

The values of discriminating power given in parentheses were obtained by considering the increase in thickness (from the final compressed thickness) after recovery instead of the total thickness. This appears to be preferable in one case, but not in the others, but the exact method of defining recovery does not affect the general conclusions to be drawn.

The striking feature of the discriminating power values is the great increase in efficiency obtained by increasing the period of compression. In comparison, differences between values for the two instruments are relatively small, and it was found that the influences of test temperature and load on results with the Defo instrument were also unimportant. Values based on recovery measurements tended to be even higher than for the longest compression period, whether based on actual thickness after recovery or on the increase of thickness

during recovery. These results are in general qualitative agreement with values reported[3] for Williams tests on a pure-gum mix in a comparison of Williams and Defo instruments. The factor of merit used there is proportional to the square root of the "discriminating power" of the present series. However, the Defo instrument was there used in its original form as a variable load instrument, resulting in some loss of efficiency in recovery measurement, so that the Defo results are not comparable with those in the present series.

To summarize, the only factor in the compression test worth varying in an attempt to improve the sensitivity to scorching is the compression period, which should be as long as possible, and recovery results are generally even more valuable. This is to be expected if scorching is thought of as preventing flow of the rubber, since prolonged compression will cause further flow of unscorched samples, but once the initial elastic deformation has occurred, relatively less flow will occur with scorched samples.

COMPRESSION TESTS: METHODS OF HEATING TEST-PIECES

The following methods, among others, have been suggested or used for preheating rubber cylinders to produce scorching.

(a) Heating in a metal mold in a bath of glycerine, water, or other liquid.
(b) Heating in a metal mold in an oven with circulating air.
(c) Heating in a tray of hot talc in an oven with circulating air.
(d) Heating, embedded in talc, in boiling tubes immersed in a liquid bath.

These four methods have been used for mixes B and C, of the following composition:

	Mix B	Mix C
Smoked sheet	100	100
Zinc oxide	5	5
Stearic acid	1	1
Zinc diethyldithiocarbamate	½	—
Tetramethylthiuram disulfide	—	½
Sulfur	2	2

Cylinders 1 cc. in volume and 11 mm. in diameter were prepared and heated at 100° C for various periods by the different methods. They were subsequently tested in the Williams plastometer at 70° C, the compressed thickness after 3 minutes and the recovered thickness after 3 minutes recovery at 70° C and 15 minutes cooling at room temperature being recorded.

Two general observations were made in the course of these tests. First, the same increase in recovery occurred for a particular increase in plasticity value, whichever method was used for the scorching, so that, although recovery values were used as a check on estimates of scorching time, only values derived from plasticity readings will be quoted below. Second, the shape and slope of the plasticity—heating period curve were, for any one mix, independent of the method of heating, the particular method of heating merely displacing the curve parallel to the time axis. This behavior would be expected if, as is believed, the rate of transfer of heat to the test-piece is the controlling factor in causing the observed differences in apparent scorch time.

Table 2 gives the period of heating at 100° C required to produce a given increase of Williams plasticity reading for the various methods. For mix B the time given was sufficient to increase the plasticity from 210 to 300 mm./100, and for mix C, from 175 to 215 mm./100.

TABLE 2

PERIODS NECESSARY TO PRODUCE EQUAL DEGREES OF SCORCHING BY VARIOUS METHODS

Method	Scorch period (min.)	
	Mix B	Mix C
(a) Preheated brass mold in water bath	13	45
(b) Preheated brass mold in air oven	—	60
(c) Tray of talc in oven	26	60
(d) Tube of talc in water bath	23	—

Method (a) produces a certain degree of scorching in 10 to 15 minutes less time than the other methods. Periods for methods (b) and (c) were even longer (by 15 minutes or more) if the air in the oven was not being circulated by a fan or, for method (b) if the mold was not preheated. However, for method (a), preheating the mold had very little influence (not more than 2 minutes) on the scorch period. It was found also that, for methods (a) and (b), the results were unaltered by changing the method of cooling test-pieces from immersion of the mold and contents in cold water to removing the test-pieces and dropping them into water.

Thermocouple measurements showed that the mold fell in temperature from 100° to 75° C on being removed from the oven, method (b), for a period just sufficient to insert two test-pieces; a temperature of 98° C was reached 10 minutes after its return to the oven with the air circulating, but the same temperature rise took 30 minutes when the fan was stopped. On immersion of a cold mold in the water bath, 100° C was reached within a few seconds. A thermocouple embedded in a cold test-piece did not indicate 98° C until 15 minutes after the insertion of the test-piece in hot talc in a tray in an oven at 100° C. These values are consistent with the scorch period test results. The fact that different methods of heating can give markedly different measured scorch periods means that, in comparative tests, the same method must be used consistently, and this procedure is recommended in the relevant British Standard[4].

COMPARISON OF ROTATION AND COMPRESSION SCORCH TESTS

It has sometimes been stated that Mooney or other rotation instruments give a truer picture of the likely scorching behavior of stocks during processing than do compression instruments, because the stock is being "worked" during the test. It has been shown elsewhere[1] that this is justified in the case of stocks containing reinforcing carbon blacks, and that for these stocks compression tests may be very misleading.

For gum stocks, two possible reasons have been advanced for anticipating that the Mooney scorching rate would be greater than that shown by Williams tests. The first possibility is that the stirring action might increase the rate of cross-linking, and the second is that the temperature rise in the rubber during test due to shearing the viscious material might accelerate scorching, as it does in processing rubber stocks.

Figure 1 shows the scorching curves obtained for mix A, (1) with the Williams plastometer, using method (d) of the previous section, for either compressed thickness (5 minutes' compression of 1-cc. test-piece at 70° C) or, recovery, i.e., increase in thickness (8 minutes' recovery at room temperature after the above compression), and (2) with the shearing-cone plastometer.

The shearing-cone (modified Mooney) instrument[5] was used at 100° C at a shear rate of 1.0 radian per second, a rate corresponding approximately to the mean shear rate in the Mooney instrument; the torque, in arbitrary units, required to turn the rotor is plotted against the period after closing the plastometer dies. The motor was started 1 minute after closing the dies. The general form of the curve is similar in all cases; taking into account the delay in raising the compression test-pieces to the scorching temperature in method (d), and the short period (2–3 minutes) required to heat the shearing cone plastometer sample, the results are consistent with the assumption that neither of the effects discussed in the previous paragraph is important in the present case.

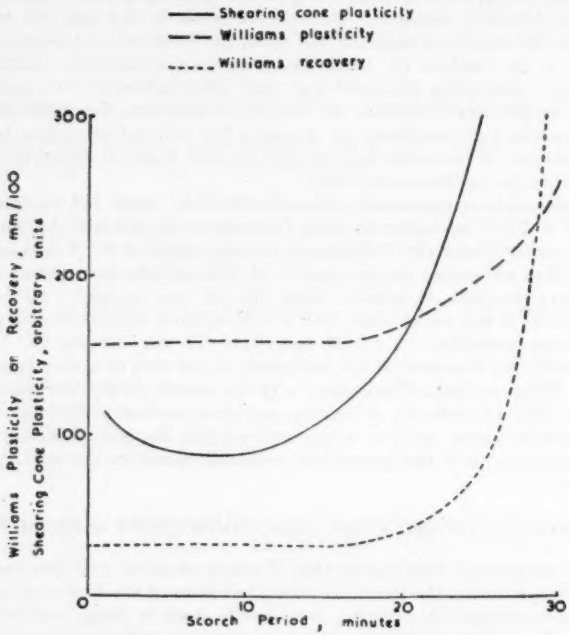


FIG. 1.—Comparison of shearing-cone and Williams scorch curves.

Similar correlation of rotation and compression test results has been obtained on other non-black stocks.

From results in a previous report[6] a temperature rise of about 2° C at some points in the rubber might be expected in a Mooney test on a sample of Mooney viscosity 40 (large rotor), but the average temperature rise would be much less and of little importance. In this connection, it seems probable that the very short "Tuber scorch times" (compared with Mooney times) quoted in several papers[7] are caused by local high temperatures in the extruder, and should not, without further investigation, be regarded as evidence that certain compounds have a scorch rate more sensitive to shearing than others with the same Mooney scorch period.

SUMMARY

It is shown that the main factor influencing the efficiency of compression plastometers in detecting scorching of a pure-gum rubber mix is the period of compression; this should be at least five minutes for the Williams plastometer at 70° C. Recovery measurements appear to have an even higher efficiency than long period compression tests. Other variations of test conditions are not of great importance. The next point examined is the method of producing scorching in compression test-pieces. Immersion of test-pieces, contained in a metal mold, in a liquid bath gives the most rapid heating. Finally, it is shown that for pure-gum mixes, compression and rotation plastometers give equivalent data, provided that allowance is made for any delay in the heating of test-pieces used for compression tests.

REFERENCES

[1] Whorlow, R. W., unpublished experiments.
[2] Newton, Scott, and Whorlow, *Proc. Intern. Rheological Congress*, The Hague, 1948, pp. 11–204, 111–61.
[3] Whorlow, *J. Rubber Research* 18, 51 (1949).
[4] British Standard, B.S. 1673, Part 3.
[5] Piper and Scott, *J. Sci. Instruments* 22, 206 (1945).
[6] Whorlow, *J. Rubber Research* 20, 39 (1951); RUBBER CHEM. & TECHNOL. 25, 387 (1952).
[7] See, for example, Drogin, Bishop, and Wiseman, *Rubber Age* (N. Y.) 64, 309 (1948).

COMPARISON OF ROTATION, EXTRUSION, AND COMPRESSION PLASTOMETERS *

R. W. WHORLOW

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

INTRODUCTION

The majority of the instruments which have been used from time to time to measure the "plasticity" of rubbers and rubber stocks may be classed as being of the compression, rotation, or extrusion type. In this investigation an attempt was made to compare the performances of representative instruments of each type in various respects. First, the discriminating powers of these instruments in distinguishing between smoked sheet samples masticated for different periods, or between carbon black masterbatches milled for different periods, were compared. Second, the sensitivities of the methods to structure in carbon black stocks were determined. Finally, the relationship between rotation and extrusion results was considered, and the relative advantages of the instruments for various applications compared.

The Dillon plastometer[1], which is designed for the routine control of the plasticity of factory mixes, and is robust, foolproof, and easy to operate, was taken as a representative extrusion instrument. The test consists of forcing a standard volume (5.5 cc.) of stock through a die (4.8 mm. long, 3.2 mm. diameter) at 80° C, and determining the time required. The rubber is contained in a chamber above the die, and a steel piston is forced by air pressure into the chamber, the displaced rubber passing through the die. The air pressure is adjusted to a value suitable for the type of material being tested, and a preheated sample is loaded into the machine. On closing the die cavity, all subsequent operations occur automatically, and the extrusion time is read off directly from an electric stop-clock. The actual pressure on the rubber is 86 times the air pressure.

The rotation instrument used was the shearing cone plastometer of Piper and Scott[2]. This is similar to the Mooney shearing disc viscometer, but uses a biconical rotor in place of the disc; the usual Mooney temperature of 100° C was used.

These instruments were compared with a standard Williams compression plastometer[3] operated at 80° C. This instrument has been compared previously with other compression plastometers[4].

DISCRIMINATING POWER

Samples of blended smoked sheet masticated for various periods on a laboratory mill, and samples of a smoked sheet/MPC black (100/50) masterbatch remilled for various periods, were tested. The mean plasticity values obtained are given in Table 1. The conditions of test are given.

* Reprinted from the *India-Rubber Journal*, Vol. 125, No. 5, pages 174–178, August 1, 1953. The present address of the author is the Battersea Polytechnic, London, England.

Dillon.—Samples preheated 6 min. in press at 85° C and 20 sec. in plastometer at 80° C; test temperature 80° C; air pressure 12 lbs. per sq. in. (black masterbatch) or 5 lbs. per sq. in. (smoked sheet); extrusion period quoted in sec.

Williams.—1-cc. test-piece; 5 kg. load; test-pieces preheated 15 min. in oven; temperature 80° C; 3 min. compression period; compressed thickness quoted in mm./100.

Shearing cone.—Samples preheated 1 min. in plastometer; temperature 100° C; shear rate 1.0 rad. per sec.; reading of torque after 4 min. shearing, quoted in arbitrary units.

TABLE 1

MEAN PLASTICITY VALUES FOR VARIOUS TESTS

Masticated smoked sheet				Remilled black masterbatch			
Mastication period (min.)	Dillon extrusion 80° C (sec.)	Williams compression 80° C (mm./100)	Shearing cone rotation 100° C (arbitrary units)	Remill period (min.)	Dillon extrusion 80° C (sec.)	Williams compression 80° C (mm./100)	Shearing cone 100° C (arbitrary units)
5	72	252	228	5	13.2	337	297
10	18.7	202	171	10	7.6	324	279
15	13.9	189	152	15	7.2	308	255
20	10.5	183	142	20	5.1	301	228

Note.—The carbon black-loaded samples were tested using a rotor and die cavity geometrically similar to that described by Piper and Scott[2], but on a smaller scale. Readings have been multiplied by 3 to give values comparable to those with the standard rotor.

Each value in Table 1 is the mean of four replicate measurements. From an analysis of variance carried out on the results of each type of test it is possible, in the manner described by Newton, Scott, and Whorlow[4], to determine the relative discriminating powers of the tests, and factors calculated in this way are given in Table 2. The discriminating power is defined as the ratio of the variance "between rubbers" to the variance "within rubbers", and is inversely

TABLE 2

RELATIVE DISCRIMINATING POWER OF PLASTICITY TESTS

	Masticated smoked sheet	Remilled black masterbatch
Dillon	0.2	2.8
Williams	1.0	1.0
Shearing cone	0.9	1.4

proportional to the number of replicate tests necessary to achieve a given accuracy of test with each instrument. Results are given relative to the Williams discriminating power as unity. The Dillon value is based on the logarithm of the extrusion time, as the standard deviation of results on one rubber is approximately proportional to the mean extrusion time.

The carbon-black masterbatches were tested after approximately equal periods of storage after mixing, to avoid differences in the amount of carbon black structure present (see the section on "Carbon Black Structure").

Considering first the results for masticated smoked sheet, it is clear that the Williams and shearing-cone instruments have very similar discriminating

powers, but that the Dillon instrument is much inferior, a conclusion confirmed by an independent series of tests. For the black masterbatches, the Dillon instrument appears to be more efficient than either shearing-cone or Williams instruments, but there is reason to believe that the shearing-cone plastometer results were abnormally variable in this series. The coefficient of variation for replicate tests was higher than is normally encountered in tests on black loaded stocks. For example, Table 3 gives the coefficient of variation (standard deviation as a percentage of the mean value) estimated for the various instruments from the above results, and also the values obtained in an independent series of eight replicate tests of a black masterbatch on the three instruments.

These results, taken in conjunction with those in Table 2, suggest that the Dillon and shearing-cone instruments have similar discriminating power for black stocks, with the Williams instrument inferior.

It is interesting to note from Table 3 that the coefficient of variation of Dillon results is much less for the black masterbatch than for the smoked sheet samples, whereas the reverse is true for Williams results, and this largely accounts for the difference in discriminating power of the Dillon relative to the Williams for the two types of rubber. The greater variability of smoked sheet

TABLE 3

COEFFICIENT OF VARIATION FOR TESTS ON VARIOUS INSTRUMENTS

	Masticated smoked sheet	Carbon black masterbatch	
	Mean for samples in Table 1	Mean for samples in Table 1	Value from 8 replicate Tests
Dillon	15	8	8
Williams	1	2	2
Shearing cone	2	3	1

results for the Dillon instrument is probably associated with the very uneven appearance of the extruded thread in this case, since this suggests irregular extrusion, so that small differences in consistency or test procedure would be expected to influence the extrusion rate considerably.

To sum up, the Williams and shearing-cone instruments are both superior to the Dillon, by a considerable factor, in assessing the extent of smoked sheet mastication, but the Dillon and shearing-cone instruments are both superior to the Willimas for controlling the remilling of carbon black loaded stocks.

CARBON BLACK STRUCTURE

It has been shown that the stiffening of carbon black-loaded stocks on storage, due to the formation of some kind of structure which can be broken down by subsequent shearing, may seriously interfere with plasticity tests[6]. The following measurements were made to compare the relative susceptibilities of the tests to interference from this source.

Samples of the MPC black masterbatch used in Section 2 were heated for 1 hour at 100° C in order to accelerate the stiffening which occurs slowly at room temperature. Four replicate test-pieces of each heated sample were tested by each of the three methods; the mean plasticity values are recorded in Table 4. The ½-minute and 1-minute shearing-cone values read from smoothed

TABLE 4

MEAN PLASTICITY VALUES FOR UNHEATED AND HEATED CARBON BLACK MASTERBATCHES

Treatment	Sample	Remilling period (min.)	Dillon (sec.)	Williams (mm./100)	Shearing cone (arbitrary units) 4 min.	½ min.	1 min.
Preheated	A	5	37	404	321	453	432
	B	10	19	389	288	417	408
	C	15	16	365	285	411	396
	D	20	12	357	249	375	360
Unheated	A	5	13.2	337	297	375	363
	B	10	7.6	324	279	360	342
	C	15	7.2	308	255	330	312
	D	20	5.1	301	228	297	282

torque/period-of-shearing curves are also given, for reasons mentioned below, but should not be regarded as accurate indexes of plasticity as the results are rather variable.

In all cases the heated samples are stiffer, but the degree of stiffening differs considerably from test to test. From the Dillon results, the softest sample, D, appears after heating to be almost as stiff as the hardest sample, A, unheated. By the Williams test, the heated sample D is much stiffer than the unheated sample A, but by the shearing-cone method (4 min. value) the heated sample D is much softer than the unheated sample A. Thus the presence of carbon black structure is most likely to lead to wrong conclusions in the Williams test, and is least troublesome with the shearing-cone (4 min.) test.

It has been shown[6] that a rough guide to the degree of structure breakdown is given by the work done on unit volume of rubber. Taking values for the heated sample D as an example, the following estimates of the work done on 1 cc. of rubber in each test may be made.

Dillon.—Pressure on rubber = 7.1×10^7 dynes/sq. cm. Work per unit volume rubber = 7.1 joules.

Williams.—5-kg. load falls 0.7 cm. approx. Work per unit volume rubber = 0.34 joule.

Shearing cone.—Mean shear stress over 4 min. = 1.5×10^6 dynes/sq. cm. Shear rate = 1.0 rad./sec. Work per unit volume rubber = 36 joules.

From these values we should expect the Dillon instrument to be intermediate in behavior between shearing-cone and Williams instruments in its sensitivity to carbon black structure, as is observed. However, reducing the period of shearing in the rotation instrument to about ¾ minute would be expected to reduce the degree of breakdown to about that in the Dillon instrument, and the final columns in Table 4 show that for the shorter shearing periods, the heated sample D has a similar stiffness to the unheated sample A. In view of the widely different shear rates, and the different temperatures, this close agreement with the anticipated results is probably fortuitous, but the "work" concept appears to give an approximately quantitative explanation for the difference in behavior of the instruments.

CORRELATION BETWEEN DILLON AND SHEARING-CONE RESULTS

The problem of correlating extrusion and rotation plastometer results may be approached in two ways. We may either attempt to derive a stress/strain-rate curve for a rubber from both sets of data, and compare these, or else simply

attempt to correlate the actual test results by the two methods for different types of stock. Both approaches are considered in turn below.

The first method is only possible if certain assumptions are made about the geometry of the extrusion die, and the behavior of the rubber, and can be used approximately for masticated smoked sheet, but not for carbon black loaded stocks.

One sample of masticated smoked sheet was tested with various pressures of air with the Dillon instrument and at various rates of shear in the rotation plastometer. In each case a stress/strain-rate relationship was deduced, using for the extrusion results a procedure given by Burgers[7], based on the assumptions that the shear stress is a function of rate of strain only, that no slippage occurs at the walls of the die, and that end effects are negligible. The results determined are plotted in Figure 1. Unfortunately, the ranges of strain rate of the two instruments do not overlap, but a reasonable extrapolation of the shearing-cone data—the most reliable in view of the above assumptions in calculating the extrusion values—suggests that the force required for extrusion is greater

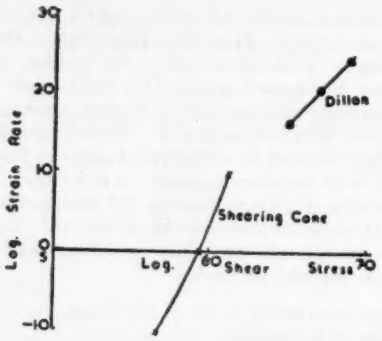


FIG. 1.—Stress/strain-rate curves from rotation and extrusion plastometers.

by a factor of two or three than would be anticipated from the properties of the material in bulk. This result can be accounted for by the force necessary to deform the rubber prior to passing through the die and the various simplifying assumptions made. There is no evidence for slippage of rubber, which would reduce the force required to extrude at a particular rate, but there is no positive evidence that slippage does not occur.

The factor preventing the use of the rotation instrument at higher shear rates is the excessive temperature rise which would occur in the rubber. Owing to the short time during which the rubber is being sheared, the temperature rise during the extrusion test is probably not more than 1°–2° C at the highest pressures used in these tests. This possibility of using high shear rates may be one important advantage of extrusion instruments, since shear rates in processing operations are high. However, a detailed study of the effects of varying tube length, diameter, etc., would be necessary before much reliance could be place on calculated stress/strain-rate relationships.

In order to compare the Dillon extrusion time at a constant air pressure (5 lb. per sq. in.) with shearing cone plastometer results under standard conditions (reading in arbitrary units after 10 minutes of shearing at 0.1 radian per second),

results were obtained for samples of masticated smoked sheet containing no filler, and for samples containing 50 parts MPC black. Figure 2 shows that results for the two sets of samples are grouped about separate lines, the black-loaded samples giving a larger shearing-cone reading at a particular Dillon extrusion rate. This may be due to the low shear rate in the shearing-cone tests, since as the shear rate is raised there will be a tendency for the black-loaded stocks to soften relative to the smoked sheet[8] so that the two curves would tend to approach each other.

It will be noticed that the sample with a loading of clay (100 parts) groups with the unloaded samples. Of greater interest is the position of points corresponding to smoked sheet or black masterbatch into which four parts of pine tar had been incorporated (points marked P in Figure 2) and the point (S) corresponding to masticated smoked sheet compounded with stearic acid (2 parts). In all cases the points remain near the appropriate line, showing that the effect of the softeners is similar to that of mastication. There is no

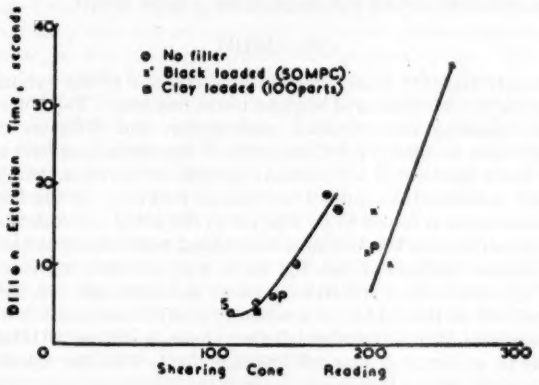


FIG. 2.—Correlation of Dillon and shearing-cone plastometer results.

tendency for extrusion rate to be increased relative to the value anticipated from shearing-cone data, as would be the case if the softeners caused or increased slippage of rubber over the wall of the extursion die.

DISCUSSION

In studying the properties which are important in influencing the extrusion behavior of rubbers, both the plastic properties of the bulk material and the possibility of slippage over smooth surfaces under some conditions must be considered. In the shearing-cone and Williams plastometers, care is taken to eliminate slippage effects so that the properties of the bulk material are measured. In the Dillon extrusion test, it is possible that slippage might influence the result. However, it is unlikely that the relative contributions of slippage and true flow to the amount of material extruded would be the same in the instrument as in a factory size extruder so that the possible gain in usefulness may be small. The instrument might, for example, give too great an emphasis to the slippage aspect. A detailed study of the instrument on a wide range of

materials of known processing behavior would be necessary before this question could be settled with any certainty.

Considering the Dillon instrument simply as a method of determining the bulk plasticity of samples, we may compare it with the shearing-cone and Williams instruments. It seems clear that the rotation type instrument—it may be assumed that the Mooney viscometer would yield results very similar to the shearing-cone instrument—is the best general purpose plastometer. For uncompounded masticated smoked sheet, the Williams instrument has similar efficiency, but the Dillon instrument is much inferior. For black masterbatches, the Dillon may have a greater power of discriminating between samples remilled for different periods, but is more sensitive to carbon black structure. The Williams plastometer is not very useful for such materials.

It should be emphasized that this picture is incomplete, and the Dillon instrument may, due to the high shear rate and extrusion principle, be superior to the rotation instruments in correlation with processing behavior. This aspect does not come within the scope of the present report.

SUMMARY

Instruments expected to give results characteristic of the various classes of plastometer have been compared in a number of respects. The Dillon extrusion plastometer, shearing cone rotation plastometer, and Williams compression plastometer, were compared for their power of discriminating between samples of smoked sheet masticated for different periods, or between samples of MPC carbon black masterbatch remilled for various periods. In the first case, the Dillon instrument was found to be inferior to the other instruments, while for the black masterbatches the Williams instrument was inferior to the other two.

The Williams instrument was the most, and the shearing cone the least, influenced by carbon black structure, a result in agreement with the use of the energy expended on the rubber as a measure of structure breakdown.

Consideration of the correlation between shearing cone and Dillon plasticity values gives no evidence of marked slippage effects with the extrusion instrument, although it cannot be shown conclusively whether or not slippage occurs with the present form of instrument.

It is concluded that a Mooney or shearing cone instrument is probably the best for general use, but that the Dillon instrument may have advantages for tests on carbon black loaded stocks.

ACKNOWLEDGMENT

We are pleased to take this opportunity to thank the Firestone Tyre and Rubber Co., Ltd., for permission to carry out the work described on the Dillon plastometer in the Company's laboratory.

REFERENCES

[1] Dillon and Johnston, *Physics* **4**, 225 (1933); Dillon, *Physics* **7**, 73 (1936).
[2] Piper and Scott, *J. Sci. Instruments* **22**, 206 (1945).
[3] Williams, *Ind. Eng. Chem.* **16**, 362 (1924).
[4] Newton, Scott, and Whorlow, *Proc. Intern. Rheological Congr.*, The Hague, **1948**, II-204, III-61.
[5] Mullins and Whorlow, *Trans. Inst. Rubber Ind.* **27**, 55 (1951); Whorlow, R. W., unpublished experiments.
[6] Mullins and Whorlow, *Trans. Inst. Rubber Ind.* **27**, 55 (1951).
[7] Burgers, "First Report on Viscosity and Plasticity", Amsterdam, p. 89.
[8] Mullins and Whorlow, *Trans. Inst. Rubber Ind.* **27**, 55 (Fig. 7) (1951).

STUDY OF THE FACTORS AFFECTING THE FRICTION OF TREAD COMPOUNDS ON ICE *

C. S. WILKINSON, JR.

RESEARCH DIVISION, GOODYEAR TIRE & RUBBER CO., AKRON, OHIO

Experiments to study the frictional properties of rubber on ice have consisted almost entirely of tests upon tires mounted on motor vehicles; ice or snow covered highways and frozen lakes were the laboratories. Although these experiments have the advantage of similarity to normal conditions of use, they suffer from uncontrollable variables such as sudden changes in temperature, deterioration of the ice surface, and capability of the driver. It is not uncommon in slide-to-stop tests to have a range of two to one in the distances necessary to stop a car or truck in successive trials over the same course. Such variability occurs for tests with both synthetic and natural rubber tires.

A more sensitive laboratory test in which the variables could be carefully controlled would seem to be most useful. Little has been published concerning such tests. Conant, Dum, and Cox[1] measured both static and dynamic coefficients of friction for a number of compounds. They used an apparatus in which the test-piece was repeatedly drawn along a linear path at a velocity of 0.48 foot per second. The coefficient was calculated from an average value of the frictional force. More recently Pfalzner[2] described experiments using a machine in which a circular track of ice was revolved against sled-like rubber samples. The samples were lightly loaded and were run at velocities of up to 12 feet per second. In both these experiments the entire apparatus had to be used in a cold room, which resulted in a limited range of temperatures and difficult working conditions for the operator.

In setting up the present experiment, the aim was to be able to control the experimental variables closely and yet be able to change conditions at will over a wide range. It was decided to design a compact machine which could be placed in a laboratory subzero cabinet for operation. In this way the temperature could be varied over a wide range, but held within close limits at any desired point. The operator, being outside and at room temperature, could work more comfortably and make accurate observations more easily.

APPARATUS

A diagram of the apparatus is shown in Figure 1. The ice is frozen in an aluminum tray which revolves under the stationary samples. The outside diameter of the tray is one foot. On each leg of the tripod above the ice tray is an adjustable brass slider counterbored to hold a sample. These sliders may be adjusted rapidly to determine the path of the samples. Weights for vertical loading slip down over the center post and rest upon the tripod.

The oil-filled sylphon bellows and the pressure gauge are ordinarily used to measure the frictional force. For several special experiments they were re-

* Reprinted from the *India Rubber World*, Vol. 128, No. 4, pages 475–481, July 1953. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at the meeting of the Division at Buffalo, N. Y., October 29–31, 1952.

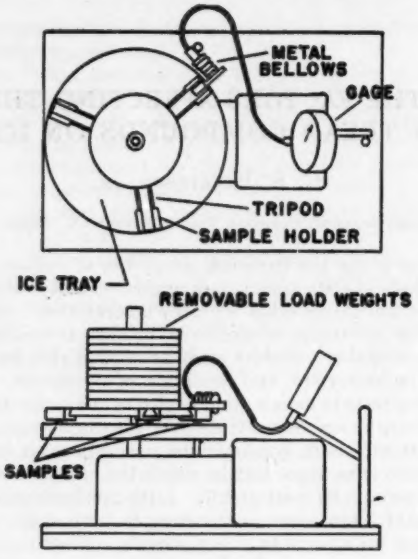


FIG. 1.—Diagram of apparatus.

placed by a strain gauge recording element and bridge arrangement. As the ice tray revolves, the tripod, with samples in contact with the ice surface, tends to move with it, but is restrained by the reaction of the bellows against one leg. This reactive force is indicated as pressure on the gauge, and can be converted

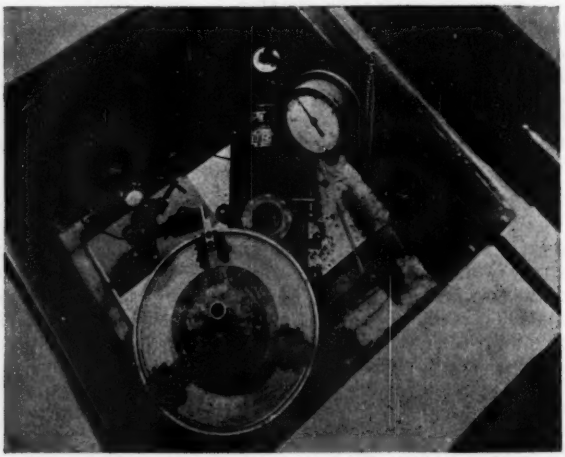


FIG. 2.—Photograph of apparatus while in operation.

into frictional force by multiplying by the effective cross-sectional area of the bellows.

The vertical load is the weight of the tripod and samples, six pounds, plus any added weights.

The mechanism for turning the ice tray is a commercial variable speed drive, with a micrometer adjustment for varying its velocity continuously over the range from zero to 118 r.p.m.

Figure 2 is a photograph of the apparatus while in operation The cover of the subzero cabinet has been removed temporarily to allow the photograph to be made.

METHOD OF FREEZING ICE FOR USE IN FRICTION EXPERIMENTS

Variations of friction due to differences in ice crystals may be minimized by carefully freezing the ice according to a definite procedure. Aside from having uniformity of crystal structure, it is desirable that the ice be: (1) transparent; (2) flat and level; (3) crack-free.

Air bubbles in the ice are to be avoided if the surface is to be uniformly smooth. Concentrations of air bubbles will modify the friction in spots where they are present. Flatness and levelness are necessary for steady gauge readings. Although fine cracks cause no trouble themselves, there is a tendency for the ice to chip in the vicinity of a crack, producing an uneven surface.

The exact procedure used in preparing the ice for these experiments will be described for the benefit of those who may be beginning similar experiments. First, the aluminum tray from the apparatus was placed in a $-29°$ C cold room at least one-half hour before filling. Distilled water, meanwhile, was boiled five or ten minutes in a filter flask to drive out dissolved air; then the flask was stoppered while still containing only vapor above the water. The flask containing water and vapor was placed in a bed of dry ice until ice crystals began to form on the inner walls of the flask, indicating that the mass of water was at about 0° C.

The stopper was then removed, and the chilled water poured into the cold tray. Both were left in the cold room at $-29°$ C for several hours until the water was completely frozen. During this interval, some air from the room was invariably absorbed, but the bubbles formed were generally close to the surface and could be subsequently removed.

Flattening and leveling of the surface was done after the try had been transferred back to the laboratory low-temperature cabinet. For this operation, auxiliary apparatus was added to the original machine. To a rigid steel rod screwed into the base and projecting vertically beside the ice tray and several inches above it was hinged a steel bar extending horizontally over the ice and directed radially toward the center of the tray. (The hinge was merely a V-type laboratory clamp resting on an adjustable collar around the vertical rod.) A sharp tool bit was held securely in place at the end of the bar by means of a C-clamp. This bit could be adjusted downward to make contact with the ice surface. The ice could be "faced off" smooth and level by slowly moving the tool across its surface while the tray revolved at a high speed, about 115 r.p.m. The tool was moved by rotating the horizontal supporting bar about the hinge joint. After each cut, the tool bit was lowered a few thousandths of an inch to make the next cut.

Finally, a glass-smooth surface was obtained by placing an infrared heat lamp just above and to one side of the tray and rotating the tray at a slow speed,

just fast enough to allow a very thin film of water to be melted. Refreezing took place during the part of the revolution when the melted ice was on the side not directly under the lamp. Cracks, which invariably occurred when the temperature was reduced to below −40° C, were mended by raising the cold box temperature to slightly below 0° C and using the lamp in the above manner.

Refacing could be done at any time during a series of tests. Whenever the ice had been reworked to a point where about half of it had been used up, the tray with its remaining ice was returned to the −29° C room, and water added to restore the original level. The thin layer of ice already in the tray seemed to facilitate freezing of new ice, possibly by furnishing nuclei.

With careful use, a tray of ice could be made to last several weeks, with only occasional reworking to be sure of an uncontaminated surface. Between tests, the ice surface was carefully covered to minimize condensation and freezing of atmospheric moisture on the surface.

COMPOUNDS USED

The compound formulas used are given in Table 1.

TABLE 1

COMPOUND FORMULAE USED

	A	B	C	D	E	F	G	H	I
GR-S X445 (cold rubber)	100								
GR-S-10		100							
GR-S			100		100	100	100	100	100
Smoked sheet				100					
HAF (Philblack-O) carbon black	50	50	50	50	20	35	50	60	
MT (Thermatomic) carbon black									60
Zinc oxide	5	5	5	5	5	5	5	5	5
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
Amax (Vanderbilt)	.75	.75	.75	.75	.75	.75	.75	.75	.75
Diphenylguanidine	.25	.25	.25	.25	—	—	—	—	.25
Phenyl-beta-naphthylamine	—	—	—	—	.25	.25	.25	.25	—
Stearic acid	—	—	—	1.0	1.0	1.0	1.0	1.0	1.0

CALCULATION OF COEFFICIENT OF FRICTION

The coefficient of friction, k, is calculated as the ratio of the frictional force, F, to the vertical load, L, according to the equation:

$$k = \frac{F}{L}$$

For many materials, k is constant over a wide range of experimental conditions. In the case of rubber sliding on ice, it proves to be a variable, depending on the pressure, velocity, and temperature. The above equation may be more properly written, therefore, as:

$$F = f(P, v, T)\, L$$

where P is the pressure of the rubber on ice, v is the velocity, and T the temperature.

TEST VARIABLES

Results may be influenced to some extent by factors unique to the apparatus or type of test. In this category may be included: (1) type of sample used; (2) velocity of sliding; (3) path of sample; (4) method of applying load. These variables were studied, and the degree of reproducibility was examined.

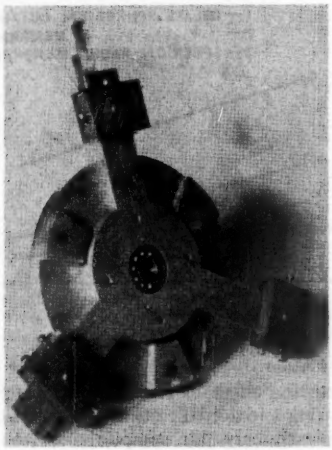


FIG. 3.—Samples in tripod holder.

Several shapes of test-pieces were tried during the course of the various experiments. A rubber cylinder, ½-inch high by ½-inch in diameter, was first used. When the cylinder was inserted in the counterbored holder, ⅛-inch of its length projected. Both sharp and beveled edges were checked. Such a sample has the advantage of being easy to make and in many cases gives reproducible results. It has the disadvantages of occasionally picking up ice

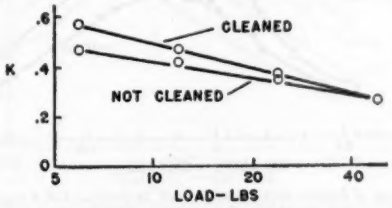


FIG. 4.—Effect of cleaning sample surface (temperature, −20° C; GR-S tread C; cure, 55 minutes at 275° F).

crystals on its contact face and also of tending to vibrate under certain conditions. This vibration is particularly noticeable with softer compounds.

A flat disk of rubber, ½-inch in diameter and 0.060-inch thick, cemented to the end of a ½-inch diameter metal cylinder, proved an improvement in the matter of vibration. It still was objectionable, however, for picking up ice crystals on its face.

A modification of the last sample has been quite satisfactory. The disk is molded into the shape of half of an oblate spheroid, with a maximum thickness of 0.1 inch. The photograph of Figure 3 shows three of these samples in place in the tripod. Vibration is greatly reduced, and picking up of ice is practically eliminated. Samples have been used just as they are when removed from the mold, and also after light buffing with Crocus cloth. Figure 4 shows results of

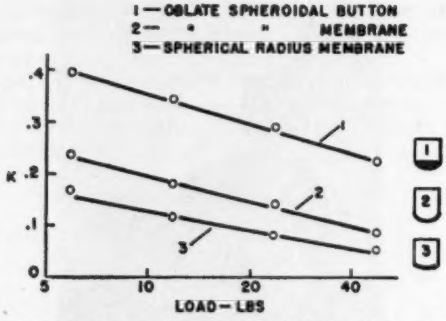


FIG. 5.—Effect of sample shape and thickness (temperature, −20° C; GR-S tread C; cure, 55 minutes at 275° F).

an experiment to study the effect of this buffing. Any bloom which occurs between the time of curing and actual testing is also removed by the buffing.

The effect of using extremely thin samples is shown in Figure 5. Here a molded button, 0.1 inch thick, is compared with membranes of identical rubber stretched tightly over metal plugs. The plug used for the middle curve was shaped very nearly like the molded button; while the plug used for the bottom curve was an exact spherical shape having a radius of curvature of ½ inch.

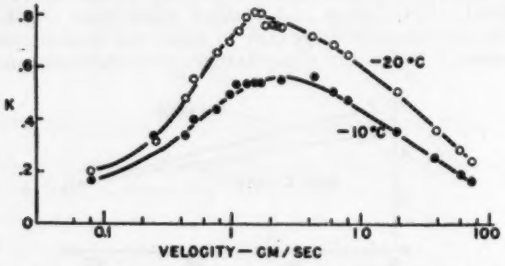


FIG. 6.—Change of friction with velocity (load, 24 pounds; GR-S tread F; Cure, 20 minutes at 300° F. Log scale—Velocity axis).

The membranes in both cases were about 0.002 inch thick. The reduction in the frictional force shown with these membranes is believed to be due to their inability to maintain intimate contact with the ice surface.

All data for Figures 6 through 18 were obtained using the oblate spheroid type of test-pieces.

The contribution of velocity to the variation of the frictional force is most interesting. Figure 6 shows the changes in the coefficient of friction of a GR-S

tread compound at −10 and −20° C as the range from 0.08 centimeter per second to 70 centimeters per second is covered. A log scale was used for the velocity axis in order to spread out the low speed end. It may be seen that, in both instances, there is an abrupt rise of friction as the velocity is increased, reaching a maximum at around 2 centimeters per second; then the friction gradually declines. Part of the upper curve has been replotted on a linear scale

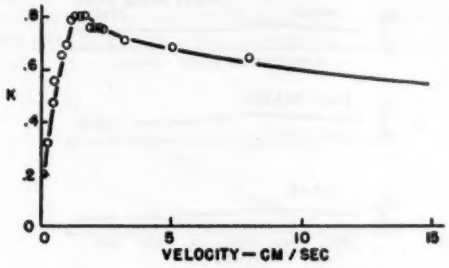


FIG. 7.—Change of friction with velocity (load, 24 pounds; GR-S tread F; Cure, 20 minutes at 300° F. Regular scale—Velocity axis).

in Figure 7 to show the abrupt rise and gradual fall in their true proportions. Figure 8 gives a family of curves to show the persistence of this effect over a range of loads, with a different type of compound used.

Practical evidence of this dependence of friction on velocity has been offered by Grace and Winter[3] in a recent publication. In describing test runs by trucks on snow and ice covered roads, these authors state that to gain maximum ac-

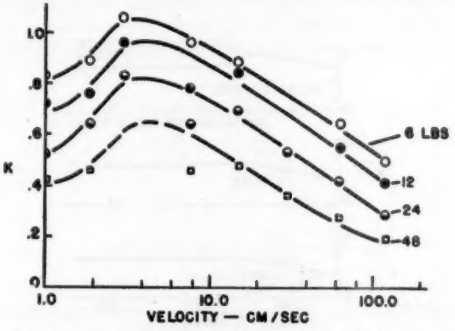


FIG. 8.—Friction as a function of velocity at several loads (temperature, −20° F; GR-S tread I; Cure, 20 minutes at 300° F).

celeration the wheels must be spun, but that excessive spinning slows down the rate of acceleration.

The special case where velocity approaches zero, that is, so-called static friction, was also studied. To make this study, the apparatus had to be considerably modified. The key between vertical drive shaft and ice turntable was removed so that the table could be revolved without use of the variable

speed drive. A music wire 0.012 inch in diameter was wound around the periphery of the turntable and led through a pulley arrangement to an external motor and reducing gear box. By this means the turntable could be started into motion without any vibration and revolved at an extremely slow velocity. The measured velocity was 0.006 inch per second, too slow to be detected by eye.

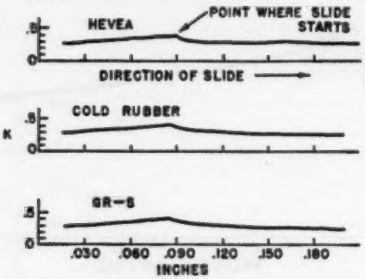


FIG. 9.—Transition from static to kinetic friction (temperature, −20° C; pressure, 30 lb. per sq. in.; velocity, 0.006-in. per sec.; standing time, 10 minutes).

To follow and measure quickly the changes in frictional force, it was necessary to use a more sensitive device than the sylphon bellows. A spring steel cantilever beam with a Baldwin SR-4 strain gauge element on each side was installed instead. The signal from this was fed into a Brush BL 320 bridge, the amplified output of which was used to actuate a BL 202 magnetic pen recorder. This equipment was capable of recording the changes in force within approximately 0.01 second.

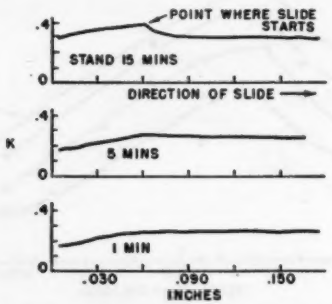


FIG. 10.—Dependence of static friction on interval of standing in contact with ice temperature, −20° C; pressure, 30 lb. per sq. in.; velocity, 0.006-in. per sec.; Hevea tread compound.

The test-pieces were placed in their mountings and precooled for ten minutes before being put in contact with the ice surface. After they had been kept standing in stationary contact with the ice an additional ten minutes, the ice tray was put into motion, and the force against the restraining spring recorded. The curves of Figure 9 show the stress build-up as the spring is deflected to the point where its reaction equals the static friction between the rubber and the

ice, the sudden drop from this maximum, and finally the steady sliding, or kinetic, friction.

In another experiment the dependent of the static friction on the interval of time for which the samples were in stationary contact with the ice was determined. Results shown in Figure 10 were obtained using a Hevea tread compound. When the contact interval was 15 minutes, the difference between static and kinetic friction was pronounced. However, as the standing time was lessened, the difference between static and kinetic friction decreased until, at one-minute standing time, it was not discernible.

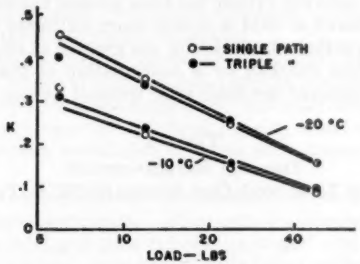


FIG. 11.—Effect of sample path (GR-S tread C; cure, 55 minutes at 275° F).

Although static friction is undoubtedly much higher than kinetic friction after standing contact for a short interval, its transient nature rules out any consideration of it as being of much importance for practical applications.

The question arises as to what effect, if any, might result from rotating the same path of ice against the samples. The most likely effect would be to reduce the friction due to a residual water film in the path. If this were the case, then staggering the samples so that they are in three separate paths should in-

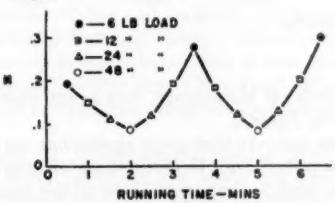


FIG. 12.—Effect of method of testing (temperature, −10° C; GR-S tread C; cure, 55 minutes at 275° F).

crease the friction. Results from such an experiment are shown in Figure 11. For very low temperatures, there seems to be no difference but, as the ice temperature approaches its melting point, the single track friction becomes slightly lower.

In actually running the test, the method of applying the vertical load and the length of time the test is run can exert considerable influence on the value of the frictional force. This point is illustrated in Figure 12. The ice was prepared in the usual way, and the tripod and the samples were put in place on

the moving ice. After one-half of minute of sliding, the pressure gauge was read, and the vertical load doubled by adding six pounds. In another one-half minute (one minute total elapsed time) a second reading was taken, and the load again doubled. At one and one-half minutes a third reading was made, and the load doubled, making a total of 48 pounds. Loads were then similarly removed in reverse order back to six pounds, after which operation the whole procedure was repeated. The samples were in sliding contact with the ice during the whole process.

As may be seen from the curve, the coefficient is approximately the same for the 48-pound load in both cycles, but shows a definite increase for the lesser loads. Apparently, once the rubber has been pressed against the ice by heavier loads, its shape is altered so that it makes more initimate contact; and subsequent values of the coefficient of friction are greater at the lighter loadings.

Reproducibility was checked by a continuation of the above experiment. The entire run was repeated one hour later without having disturbed the ice in

TABLE 2

TEST FOR REPRODUCIBILITY

Compound C GR-S Tread Stock Cure 55 min. @ 275° F. Temp. −10° C

Running time (min.)	Load (lbs.)	k_1	k_2	k_3	k_{av}	Av. dev.
0.5	6	0.198	0.198	0.176	0.191	0.010
1.0	12	0.154	0.148	0.143	0.148	0.004
1.5	24	0.118	0.107	0.118	0.114	0.005
2.0	48	0.085	0.077	0.086	0.083	0.004
2.5	24	0.132	0.099	0.132	0.121	0.015
3.0	12	0.187	0.187	0.192	0.189	0.002
3.5	6	0.275	0.275	0.275	0.275	0.000
4.0	12	0.187	0.181	0.176	0.181	0.004
4.5	24	0.127	0.118	0.121	0.122	0.003
5.0	48	0.085	0.076	0.082	0.081	0.003
5.5	24	0.138	0.124	0.132	0.131	0.005
6.0	12	0.204	0.192	0.198	0.198	0.004
6.5	6	0.308	0.286	0.286	0.293	0.010

k_1—immediately after preparing.
k_2—one hour later.
k_3—15 hours later.

any way except to brush off the surface, and again after 15 hours. Results of these tests are given in Table 2.

While these results indicate that good agreement may be obtained in duplicate tests, it should be pointed out that the same ice was used for all three runs. When different ice is used for separate tests of the same samples, variability may be greater.

TYPES OF ICE

There is a possibility that the difficulty of reproducing results may be due in part to differences in the ice itself. A brief survey of the literature indicates that investigators have from time to time observed different forms of symmetry in ice.

In 1921, Dennison[4] wrote that, as a result of x-ray diffraction studies, he believed that the lattice of an ice crystal corresponded to a hexagonal close packed arrangement of molecules consisting of two sets of interpenetrating triangular prisms with sides of 4.52 Å and height of 7.32 Å. Shortly afterward

Bragg[6], making use of Dennison's data, suggested that each oxygen atom was at the center of gravity of four neighboring oxygen atoms, from each of which it was separated by a hydrogen atom. The dimensions of the structure agreed with Dennison's figures.

Selyakov[6], experimenting with ice in constant temperature rooms at $-8°$ and $-1°$ C, showed that ice existed in two forms, alpha and beta. The former belongs to class D_{6h}, D_6, C_{6v}, or D_{3h} and the latter[7] to C_{3i} or C_3. The units of both classes are about equal, C = 7.34 Å and A = 4.52 Å. He believed that there were four molecules in each lattice. Rogers[8] at about the same time reported from a study of snow and ice crystals that ice belonged to the dihexagonal pyramidal class (A66P) of the hexagonal system. Later, Hildebrand[9] spoke of ice as having an open, continuous structure, like that of tridymite, and containing no permanent individual molecules.

Steinmetz[10] claimed that snow formed at $-12°$ C showed a prismatic habit, with thin hexagonal plates at the two ends; and he concluded that ice is probably of dihexagonal-bipyramidal symmetry, but may also be of a ditrigonal class. Finally, Frank[11] reported results of freezing water at $-72°$ C, in which octahedra and sometimes tetrahedra or cubes were formed. These melted at $-70°$ C.

Hexagonal plates, as reported by Steinmetz, have been observed in ice used in the present friction experiments. These plates appeared on a surface which had been allowed to melt and then refreeze at about $-20°$ C.

From the above survey it may be concluded that, although the types of ice crystals observed are similar, there are probabilities of obtaining differences; and these may explain at least in part the difficulty of exact reproducibility of results.

ICE AND RUBBER VARIABLES

In addition to the variables which may be thought of as being peculiar to the apparatus or method of operation are several which are characteristic of the ice and rubber themselves: *viz.*: (1) temperature; (2) pressure; (3) polymer or compound. A satisfactory explanation of the friction between rubber and ice should take these into account.

The low friction between rubber and ice is thought to be due to the lubricating action of a film of water between them. If this is the case, then as the temperature is progressively lowered, refreezing of this water will become more rapid, and the thickness of the film less. Eventually the film will become so thin that the friction will be similar to that between an ordinary smooth solid and rubber.

The curves in Figure 13, which were obtained from measurements at a series of progressively lower temperatures, show the above supposition to be correct. With the six-pound load, the friction coefficient increases rapidly to a maximum value as the temperature is progressively dropped from 0° to $-30°$ C. The curves for the heavier loads show like trends, but do not reach a maximum because the frictional forces at the lower temperatures exceed the limit of the apparatus.

After the maximum has been reached, vibration sets in between the rubber and the ice, with the result that the frictional force shows an apparent decrease as the temperature is lowered further. A similar phenomenon was reported by Roth, Driscoll, and Holt[12] as occurring with increase in velocity of rubber drawn across glass. The stick-slip mechanism responsible for the vibration will be discussed later.

Differences between tread compounds become less pronounced as the testing temperature approaches 0° C. For example, in one group of tests, a natural-rubber tread showed a friction coefficient 42 per cent higher than a similar GR-S tread when tested at −20° C. When compared at −10° C, the natural-rubber compound was only 5.5 per cent better than the synthetic. Difficulty in differentiating between various compounds in a consistent way in road tests may be due in part to temperature variations.

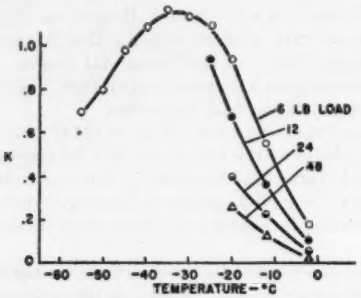


FIG. 13.—Effect of temperature (GR-S tread C; cure, 55 minutes at 275° F).

According to the classical theory of friction, the force is independent of the apparent area of contact between the rubbing surfaces, and depends only on the normal load. The explanation is that actual contact is between surface asperities and, with increase of normal load, the number of asperities in contact will increase in proportion. In the case of rubber this is only partially true. An increase of load, producing an increase of pressure, causes an increase of the frictional force, but at a decreasing rate. Consequently the coefficient, k, is

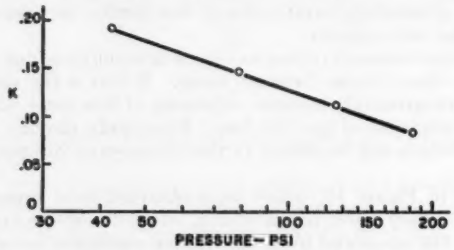


FIG. 14.—Variation of friction coefficient with pressure (temperature, −10° C; GR-S tread C; cure, 55 minutes at 275° F).

not a constant, but is a variable dependent on the value of P, the pressure. It has been found, as shown in Figure 14, that k decreases according to the logarithm of the pressure. For this particular compound the relation may be expressed mathematically as:

$$k = C_1 - C_2 \log P, \; P > 0$$

where $C_1 = .459$

$C_2 = .165$

These constants might be used as criteria of the merit of a compound. A high value of C_1 in connection with a low value of C_2 would be indicative of good frictional properties.

Carrying the above analysis a step further illustrates the practical significance of the phenomenon. The frictional force which will be obtained with a fixed load of 800 pounds at various pressures has been calculated and plotted in Figure 15. If the pressure is decreased by enlarging the area of the surface

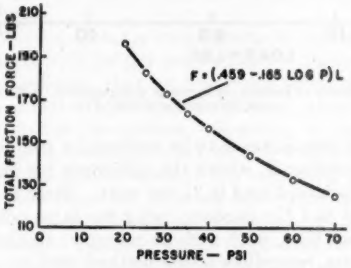


FIG. 15.—Calculated total frictional force at increasing pressure and fixed load (load, 800 pounds; temperature, −10° C; GR-S tread C; cure, 55 minutes at 275° F).

of contact, the available frictional force increases by approximately 58 per cent as the pressure changes from 70 to 20 lb. per sq. in.

The third variable to be considered is the physical or chemical properties of the rubber sample itself. Outstanding among these are the polymer used and the hardness of the cured rubber. If different polymers are compounded into the same formula and cured to the same degree of hardness, differences of their friction are observed. Figure 16 ilustrates this point for four widely differing polymers.

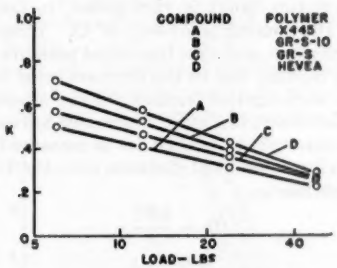


FIG. 16.—Comparison of tread compounds of different polymers (temperature, −20° C).

The matter of hardness is also of considerable importance. The spread between two samples made of the same polymer, but having considerably different hardnesses, may be greater than that for samples made of different polymers, but having the same hardness. Figure 17 gives coefficient curves for four GR-S tread compounds in which hardness was systematically varied by increasing the carbon black content.

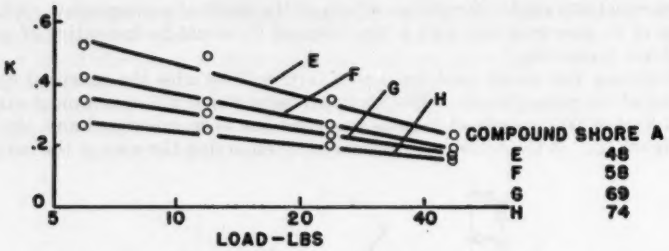


FIG. 17.—Dependence of friction on hardness (temperature, −20° C; GR-S treads; cure, 20 minutes at 300° F).

The importance of this factor may be realized by comparing this figure with that immediately preceding it, where the difference between the best polymer and the worst at a six-pound load is 31 per cent. Here the difference between the softest compound and the hardest, using the same polymer, is 49 per cent. General indications are that, with a given polymer, stocks of similar hardness have similar coefficients, regardless of the method used to vary the hardness.

THEORY

The distinguishing feature of the friction developed by a body sliding on ice, in contrast to an ordinary solid, is the film of water formed between them. This fact has long been recognized, and is the subject of considerable discussion by Bowden and Tabor[12].

The mechanism by which this water film is formed may be either pressure melting, friction melting, or a combination of both. When pressure is applied to the ice, its melting point is depressed; and if sufficient heat is supplied to the contacting object to raise its temperature to the new melting point of the ice, melting occurs. However, the pressure necessary to bring about any appreciable lowering of the melting point is very great; in fact, a pressure of 590 atmospheres represses the melting point only 5° C. Even conceding that contact occurs between asperities, and that the actual pressure is much greater than the apparent pressure, melting due to the pressure must be slight.

Melting due to the work against friction, for the moment leaving the exact meaning of the term undefined, is a more reasonable answer. If the coefficient of friction for a particular rubber against ice is measured or known, the heat generated by it in moving some fixed distance over the ice may be calculated from the following equation:

$$Q = \frac{kWl}{J}$$

where Q = heat generated (in calories).
k = coefficient of friction.
W = normal load (in dynes).
l = distance moved over ice (in centimeters).
J = Joule's constant (4.18×10^7 ergs per calorie).

By means of this equation, the data used to plot Figure 13 may now be used to calculate the amounts of heat generated per revolution of the ice tray. Results are shown graphically in Figure 18. From these it may now be seen why

the coefficient decreases as the load increases. At all temperatures as the load is increased, more heat is generated; consequently more ice is melted, producing a thicker film. This film acts as a lubricant; therefore, as it becomes thicker, the coefficient of friction becomes less.

The fact that this film exists at low temperatures may be demonstrated by stopping the ice before removing the tripod. The film of water freezes almost immediately, and the rubber is firmly welded to the ice. The bond is so firm that often a fairly large chip of ice breaks loose from the surface when the rubber is forcibly removed.

As was shown in Figure 13, a maximum value of friction is reached at some low temperature; after which, as the temperature is further decreased, friction also decreases. It is believed that, at the point where the maximum occurs heat is being lost at a faster rate than it is being generated. The rubber is momentarily welded to the ice surface, but owing to the momentum of the system and elasticity of the rubber a force quickly builds up sufficient to break the weld and allow the sample to slip into the next weld position. This stick-slip action has also been observed between lubricated metal surfaces[14]. Examination of the ice surface after a few revolutions of this nature reveals a definite stick-slip pattern. The decrease of friction at temperatures below the maximum is due to excessive vibration, which reduces intimate contact between the surfaces.

The stick-slip phenomenon gives a clue as to the fundamental nature of the friction involved. Before motion begins, there will be some asperities bearing together with sufficient pressure to melt. As other asperities assume the load, the originals refreeze, forming welded junctions. Mechanical interlocking of microscopic hills and valleys provides additional forces opposing tangential motion. When motion does begin, the welded junctions and mechanical interlocks are broken; the work is converted into heat. Ice melted by the heat quickly refreezes to form new junctions. This cycle keeps repeating as long as motion continues, forming the characteristic stick-slip pattern.

In addition to these forces, there is a slight contribution from the viscosity of the water film within the temperature range where it exists. Only very rough calculations of its magnitude can be made, but it is probably small compared to the welding forces.

In the final analysis, it may be said that friction of rubber against ice is due principally to welding and breaking of junctions, with a slight contribution from the viscosity of the water film between the sliding surfaces.

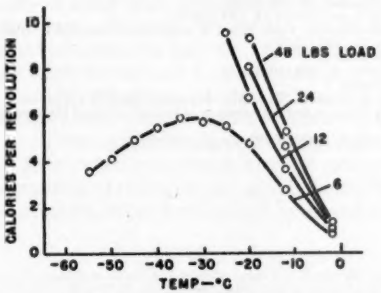


FIG. 18.—Calculated heat generated per revolution of ice tray (GR-S tread C; cure, 55 minutes at 275° F).

CONCLUSIONS

The friction of tread compounds on ice is affected to a great extent by the methods and conditions of measurement. As velocity of sliding is increased from zero to about two centimeters per second, there is an increase in friction, after which there is a gradual decrease with further increase of velocity. Static friction depends on the length of time the sample is in stationary contact with the ice, and is of little practical significance. Of the test variables studied, temperature has the greatest influence. At the lowest temperatures used, -30 to $-40°$ C, the coefficient was approximately double that usually observed slightly below the freezing point. Friction was also found to vary with pressure. An empirical equation of the form, $k = C_1 - C_2 \log P$, was found to fit results in many cases. Minor differences were noted, resulting from changes in sample shape and surface treatment.

When testing conditions were held constant, it was found that several variables in the samples themselves affected the friction. The type of polymer used had a definite effect. Of about equal importance was hardness. In similar compounds the softer samples had higher coefficients of friction.

The unusual frictional characteristics of rubber sliding on ice may be explained by taking into account the water layer formed between the sliding surfaces. The melting of ice to form this water layer takes place because of the heat generated by the work done against friction. The friction itself is believed to be caused by alternate welding and breaking of junctions between surface asperities. Although the process is initiated in part by pressure melting, that phenomenon has only minor importance after the motion is in progress.

ACKNOWLEDGMENT

The author wishes to express his thanks to the Goodyear Tire & Rubber Co. and H. J. Osterhof for permission to publish this work and to S. D. Gehman for suggestions and encouragement.

The work herein discussed was performed as a part of the research project sponsored by the Reconstruction Finance Corp., Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

REFERENCES

[1] Conant, Dum, and Cox, *Ind. Eng. Chem.* **41**, 120 (1949).
[2] Pfalzner, *Can. J. Research* **F28**, 468 (1950).
[3] Grace and Winter, *India Rubber World* **126**, 633 (1952).
[4] Dennison, *Phys. Rev.* **17**, 20 (1921).
[5] Bragg, *Proc. Phys. Soc.* (London) **34**, 98 (1922).
[6] Selyakov, *Compt. rend. acad. sci. URSS* **14**, 183 (1937).
[7] Buerger, "X-Ray Crystallography," John Wiley & Sons, Inc., New York, **1942**.
[8] Rogers, *Am. Mineralogist* **22**, 209 (1937).
[9] Hildebrand, *Science* **90**, 1 (1939).
[10] Steinmetz, *Z. angew. Mineral.* **3**, 183 (1941).
[11] Frank, *Nature* **157**, 267 (1946).
[12] Roth, Driscoll, and Holt, *J. Research Natl. Bur. Standards* **28**, 439 (1942).
[13] Bowden and Tabor, "The Friction and Lubrication of Solids", Oxford University Press, Oxford, England, 1950.
[14] Morgan, Muskat, and Reed, *J. Applied Physics* **12**, 743 (1941).

PLASTICIZATION OF RUBBER IN THE FORM OF LATEX *

MARC CONTÉ

FRENCH RUBBER INSTITUTE, PARIS, FRANCE

INTRODUCTION

The addition of peptizing agents to rubber during mastication has been widely practiced during the last fifteen years and is now an established procedure. In addition, it has been shown that peptizing agents can be incorporated in latex for the purpose of obtaining, after coagulation and drying, a softened rubber[1]. In this latter case, plasticization takes place while the rubber is being dried, an operation usually carried out around 50° or 60° C.

In the present investigation, efforts were directed toward finding out whether peptizing agents can be made to exert their action while the rubber is still in latex form; if so, rubber latex in a more or less degraded form would be expected to result.

A number of investigations have already been made with this objective in mind. In particular, latex with adhesive properties has been prepared by treatment with hydrogen peroxide[2], and plastic forms of rubber have been prepared by the action of combinations of a hydroperoxide and an activator, either on rubber in solution or on rubber in the form of latex[3].

EXPERIMENTAL TECHNIQUE

When operating with rubber in the latex form, peptizing agents which are active at temperatures below 90° C must be chosen.

Three agents, all active at 60° C, were studied, *viz.*, naphthalenethiol, xylenethiol, and zinc pentachlorothiophenate[4].

The three agents are insoluble in water, and they can be incorporated into latex only after preliminary dispersion in water. Zinc pentachlorothiophenate can be dispersed easily in a ball mill; xylenethiol can be emulsified by means of an emulsifying agent, *e.g.*, Tinnopol-NNE oil. Naphthalenethiol must be dispersed by a special technique, as follows. Twenty parts of the thiol and 2 parts of oleic acid are fused together on a steam bath, and the mixture is poured into a mixture of 10 parts of concentrated ammonium hydroxide and 70 parts of water. The ammonium oleate thus formed stabilizes the dispersion.

The dispersion of peptizing agent is added to the latex, and the mixture is heated in an oven at 70° C, then coagulated, and the rubber dried at room temperature to avoid any action of the peptizing agent during the drying operation. The degree of the plasticizing effect is measured by means of a Mooney viscometer.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 30, No. 4, pages 262–264, April 1953. The work was carried out in preparation for a final examination following instruction at the French Rubber Institute and, therefore, is not quite so comprehensive as it might have been with more time available for experimentation.

INFLUENCE OF TIME, TEMPERATURE OF HEATING, AND PROPORTION OF PLASTICIZING AGENT

The initial experiments were performed with centrifuged latex. The peptizing agent was varied from 0.4 to 1 per cent (based on the rubber), the temperature from 60° to 80° C, and the time of heating from 24 to 144 hours.

These preliminary experiments showed that there is nothing to be gained by continuing the heating beyond 48 hours or by using more than 1 per cent of peptizing agent.

However, the results were rather disappointing, for, even under the most favorable conditions, Mooney values lower than 85 degrees could not be obtained. This indicated that the effectiveness of the peptizing agent was being obstructed in some way. It was natural to feel that the ammonia might be the inhibitor, so efforts were directed toward determining any influence which it might have in the process.

INFLUENCE OF AMMONIA ON THE ACTION OF THE PEPTIZING AGENT

The ammonia was partially eliminated by first stabilizing the latex by 0.5 per cent of casein and then bubbling compresed air through the system or neutralizing with formaldehyde.

The latex mixtures containing the peptizing agent were heated for 48 hours at 80° C. In this series of tests, xylenethiol and zinc pentachlorothiophenate were tested. The results, given in Figure 1, indicate a marked inhibitory influence of ammonia.

The next step was to establish the precise nature of the influence of ammonia on the latex-thiol reaction. Rubber can be regarded as a reducing agent which is in the presence of a catalytic proportion of another reducing agent (the thiol) in the process of being transformed into the corresponding disulfide, as shown by Montu[5]. In accordance with this hypothesis, the plasticizing power depends on the mobility of the hydrogen atom of the RSH group and, consequently, of its capability of being oxidized, *i.e.*, of losing an electron in conformity with the reaction;

$$2RSH \rightarrow RS-SR + 2H + 2e$$

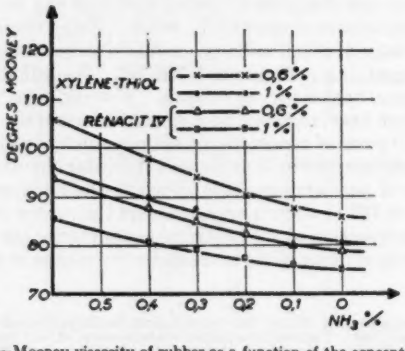


FIG. 1.—Mooney viscosity of rubber as a function of the concentration of ammonia in the latex.

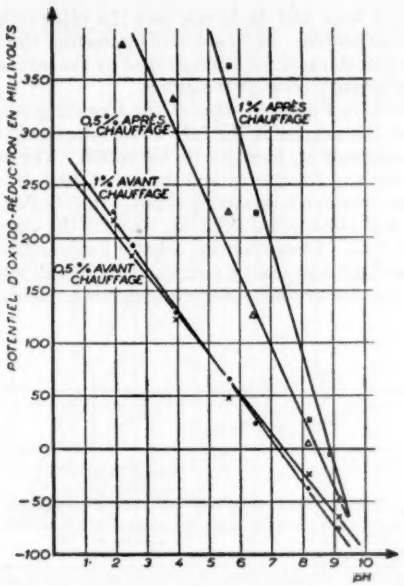


FIG. 2.—Oxidation-reduction potential of latex as a function of the pH value. (The legend of the ordinate is the oxidation-reduction potential in millivolts. On the graphs, AVANT CHAUFFAGE means BEFORE BEING HEATED; APRES CHAUFFAGE means AFTER BEING HEATED.)

Consequently, the effectiveness of such a system must be a function of the oxidation-reduction potential, and it seemed, therefore, of interest to examine in what way this potential changes with change of the pH value.

THE OXIDATION–REDUCTION POTENTIAL OF THE THIOL–DISULFIDE SYSTEM AS A FUNCTION OF THE pH VALUE OF THE LATEX

Latex, the ammonia content of which had been neutralized by formaldehyde, was first stabilized by Igepon-T (sodium oleylmethyltaurinesulfonate), and was then poured into double its volume of different buffer solutions, so chosen that the pH value would be stabilized at predetermined values between 0.65 and 9.25. To the resulting mixtures were then added 0.5 per cent and 1 per cent, respectively, of xylenethiol, and the oxidation-reduction potentials were determined before and after heating the mixtures for 48 hours at 80° C.

These oxidation-reduction potentials were determined by the potentiometric method, with a platinum electrode and a calomel electrode as a control.

The curves of Figure 2 record in summary form the results obtained and indicate a rapid decrease of the oxidation-potential and, therefore, of the oxidizing power, with increase of the pH value. This explains the unfavorable influence of ammonia on peptization.

These experiments showed the necessity of measuring the rate of transformation of thiol into disulfide. To this end, latex-xylenethiol mixtures (1 per cent of active agent based on the rubber) were adjusted, as in the preceding experiments, to different pH values, were then heated at 60° C for different lengths of

time lying between 1 hour and 48 hours, and the rates of transformation of thiol into disulfide measured. In these measurements, the amounts of thiol which had not been transformed were determined by the permanganate method, with ferrous orthophenanthroline as indicator.

The results, shown in Figure 3, support the foregoing conclusions, *i.e.*, the lower the pH value, the greater is the rate of transformation of the thiol into the disulfide. An anomaly is, however, to be noted. The curve representing the latex, the pH value of which was maintained at 10.4, is lower than any of the other curves, and its slope is relatively slight. The buffer agent used in this case was ammonia and ammonium chloride, whereas the other buffer solutions contained no NH_4^+ ions. Consequently, wholly independent of the influence of the pH value, the NH_4^+ ions exert a restraining influence which is comparable to that of amines, *e.g.*, dibutylamine, and stearylamine, during mastication with a thiol[5].

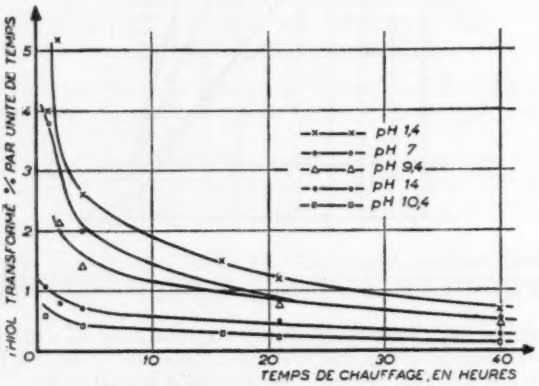


FIG. 3.—Rate of transformation of thiol. (The legend of the ordinate is the percentage of thiol transformed per unit of time; the legend of the abscissa is the time of heating in hours.)

OXIDIZABILITY MEASURED BY THE DUFRAISSE MANOMETER

The next problem of importance was to ascertain whether, under conditions which are most favorable for oxidation by the peptizing agent (in a medium of low pH value and free of NH_4 ions), oxidation of rubber is induced when it is in the form of latex. Farmer[6] has, in fact, already shown that such a phenomenon is characterized by the absorption of oxygen, which is at first rapid, then becomes very slow. Absorption measurements with a Dufraisse manometer were carried out with latex containing 1 per cent of xylenethiol and adjusted to different pH values[7]. The results, shown in Figure 4, confirm the preceding hypotheses in the sense that a decrease of the pH value, which favors oxidation of the thiol, likewise favors the induced oxidation of the rubber.

INFLUENCE OF THE pH VALUE ON PLASTICIZATION

The remaining problem was to confirm the preceding results by determining the plasticity of sheets prepared by drying, at room temperature, latex which had been adjusted to various pH values and had been heated in the presence of xylenethiol. The tests were made with latex samples having pH values of 0.8

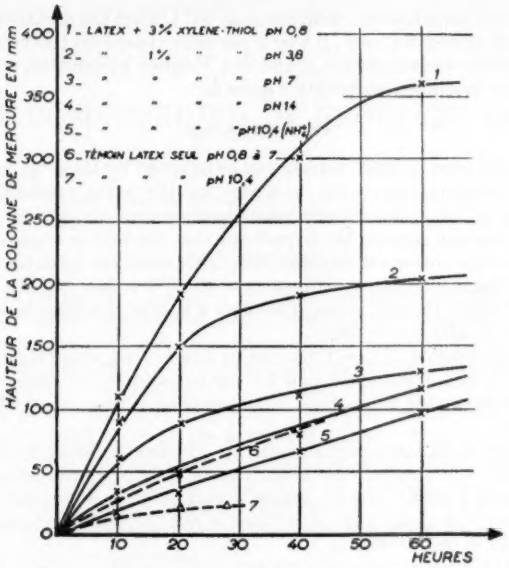


FIG. 4.—Oxidisability of latex in the presence of xylenethiol and for different pH values. (The legend of the ordinate is the height of the mercury column in mm.; the legend of the abscissa is the hours. Curve 6 is a latex containing no thiol and with pH 0.8 to 7; Curve 7 is a latex containing no thiol and with pH 10.4).

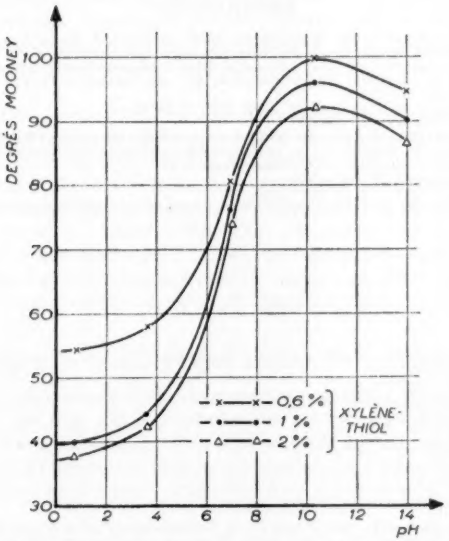


FIG. 5.—Mooney viscosity of rubber as a function of the pH value of the latex.

to 14, which had been heated for 48 hours at 80° C after the addition of different proportions of xylenethol., *viz.*, 0.6 to 2 per cent (based on the rubber).

The plasticity measurements, made in a Mooney viscometer, confirmed the preceding experimental results (see Figure 5).

CONCLUSIONS

When in the form of latex, rubber can be oxidized by thiols under hot conditions. The reaction apparently proceeds by the same mechanism as that characteristic in the action of peptizing agents on rubber during mastication. The results obtained confirm the hypothesis that the thiol is transformed quantitatively into the corresponding disulfide, with resultant oxidation of the rubbert. This transformation is a function of the pH value, and the best results are obtained when the pH value is around 4 and in the absence of NH_4 ions (which have an inhibitory effect).

Latex preparations of this type can be utilized for studying the chemical reactions of rubber in emulsion and for the preparation of rubber derivatives which are more soluble than those prepared from rubber latex which has not been degraded.

In addition, such latex preparations are excellent adhesives which, in contrast to already known products (latex treated with hydrogen peroxide or other peroxides), give a sticky film by simple drying at room temperature. In this way heating can be avoided in cases where it has harmful effects and where the use of an oven is inconvenient.

Finally, this type of latex is more adaptable to certain direct applications, both because of the superior adhesive properties of the rubber and because, with a relatively plastic coagulum, mastication is easier.

REFERENCES

[1] Wentworth, *J. Rubber Research Inst. Malaya* **9**, 90 (1939); Hastings, *J. Rubber Research Inst. Malaya* **9**, 101 (1939); British Rubber Producers' Research Assoc. and Hastings, J. D., British pat. 531,732 (1941); French pat. 867,333 (1941); British Rubber Producers' Research Assoc. and Wentworth, V. H., British pat. 536,301 (1941); Sibiriakoff, *Rev. gén. caoutchouc* **19**, 115 (1942); Cayré, *Rev. gén. caoutchouc* **28**, 276 (1951).

[2] Saint-Mleux, French pat. 979,946 (Sept. 25, 1942; Dec. 20, 1950).

[3] Kendall, *Ind. Eng. Chem.* **43**, 452 (1941).

[4] Naphthalenethiol and xylenethiol are manufactured and sold under the names of RPA no. 2 and RPA no. 3 by E. I. du Pont de Nemours & Co., zinc pentachlorophenate is manufactured and sold under the name of Renacit IV by the Farbenfabriken Bayer A.-G.

[5] Montu, *Rev. gén. caoutchouc* **29**, 506 (1952).

[6] Farmer, *Trans. Inst. Rubber Ind.* **21**, 122 (1945).

[7] The vapor pressure during the measurements was disregarded, since the measurements were only comparative ones.

TITER COMPOUNDING OF NEOPRENE LATEX *

G. S. Cook and J. C. Fitch

Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Wilmington, Delaware

INTRODUCTION

All latexes become less stable on aging, the decreased stability becoming a problem long before spontaneous coagulation occurs. Generally, difficulty is first manifested by a thickening, flocculation, or coagulation which occurs upon, or shortly after, the addition of certain compounding ingredients such as zinc oxide, curing agents, and fillers. With natural-rubber latex, this instability is considered to be due primarily to loss of volatile preservative and hydrolysis of the protective protein layer on the rubber particles. With Neoprene latexes, the primary cause is believed to be neutralization of the emulsifying system by hydrogen chloride resulting from liberation of chlorine from the polymer. Andersen and Arnold[1] have discussed this mechanism in detail. They show that the hydrogen chloride first neutralizes the free sodium hydroxide and then attacks the sodium rosinate soap layer.

It has been shown by various investigators that most of the chlorine in the polychloroprene molecule is extremely inert. However, recent work by Maynard and Mochel[2] has established that about 1.5 per cent of it is of the reactive allylic type. This chlorine, according to Andersen and Arnold[1], is readily removed by hydrolysis. Excessive exposure of the latex to air can cause the liberation of additional chlorine. Accordingly, the amount of hydrogen chloride which has formed in a Neoprene latex sample will depend upon its prior history.

Since reduction of alkalinity results in unstable Neoprene latex, a method of obtaining better stability is to maintain sufficient free alkali in the latex. This has long been recognized, and the addition of alkali has often been recommended to overcome stability difficulties, especially with older latex. In the past, the recommendations have been to add alkali until the latex or its compounds reach a given pH value[3]. However, pH measurements in the range of 11 to 13, characteristic of Neoprene latex, are insensitive, and a more accurate method of measuring and adjusting alkaline reserve would be desirable. Such a method, based on a simple titration of Neoprene latex with acid, will be described.

ANALYSIS OF NEOPRENE LATEX BY TITRATION

Titration of a mixture of strong and weak bases with a strong acid results in data which, by plotting pH against the amount of acid added, give a curve having two points of inflection. The acid required to reach the first inflection point is a measure of the strong base, while that added between inflection points is a measure of the weak base. With the basic substances in Neoprene latex,

* An original contribution to Rubber Chemistry and Technology. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Boston, Massachusetts, May 27–29, 1953.

viz., sodium hydroxide, sodium rosinate, and diethanolamine, the two inflection points occur at pH 10.5, the point at which the sodium hydroxide has been consumed, and at pH 4.5, the point at which the remaining basic substances have been neutralized. Therefore, the free alkali present in any sample of Neoprene latex can be determined easily by merely measuring the amount of acid required to reduce its pH to 10.5.

Standard laboratory equipment is used to titrate Neoprene latexes. To a 100-gram sample of latex at 25° C, one-third normal hydrochloric acid is added from a burette until pH 10.5 is attained. The pH is measured with a meter, using a sleeve-type calomel electrode and a high-pH glass electrode (Beckmann 1190E). To prevent coagulation of the latex during titration, twenty milliliters of a five per cent solution of a stabilizer[4] is added, and the latex is stirred throughout the determination. It has been found most convenient to base the titer measurement on the total weight of latex rather than on the amount of serum present, although it is realized that the important factor in maintaining stability is the concentration of alkali in the aqueous phase. Accordingly, titer is expressed as the milliequivalents of acid necessary to reduce the pH of 100 grams of wet latex[5] to 10.5.

SIGNIFICANCE OF TITER VARIATIONS

Laboratory experiments were conducted to determine the importance of titer and the practicability of utilizing it as an indication of the stability of Neoprene latex. The experiments were designed to investigate the following:

1. A comparison of pH measurement with titer measurement for following alkalinity decrease in raw latex during aging.
2. The effect of titer differences on storage stability of raw and compounded latex.
3. The effect of titer differences on the usability of latex compounds, judged by viscosities.
4. The effect of titer differences on the stress-strain properties of films prepared from latex compounds.

To evaluate the effect of free alkali content, a rather old lot of each of the general-purpose Neoprene latexes, Types 571, 842-A and 601-A, was studied over a titer range of from close to zero to approximately five milliequivalents per 100 grams of latex. The lots selected had titer values of 0.4, 1.1, and 1.2, compared with fresh latex, which is in the range of 3 to 4. From each lot a series of five samples of increasing titer values was prepared by adding, with efficient mixing, varying amounts of five per cent sodium hydroxide[6]. The amount needed to adjust to any desired titer can be calculated by means of the following equation:

$$X = 0.8\ (Y - Z),$$

where X = the weight in grams of 5 per cent sodium hydroxide to be added to 100 grams of latex,

Y = the desired titer to pH 10.5 in milliequivalents of acid per 100 grams of latex,

Z = the titer to pH 10.5 of the latex, before adjustment, in milliequivalents of acid per 100 grams of latex, and

0.8 = the reciprocal of the normality of a five per cent solution[6] of pure sodium hydroxide.

For tests involving compounded latex, the following dry recipe was used:

Neoprene from latex	100
Zinc oxide	5
Neozone-D	2
Hard clay	10
Aquarex-SMO	3

The latex samples and the compounds prepared from them were aged in tightly closed glass containers at room temperature and, to accelerate changes, in ovens at 39°, 50°, and 70° C.

The first objective of this work, a comparison of pH measurement with titer measurement for following alkalinity decrease in raw latex during aging, was attained by periodic determination of the pH and titer of the raw latex samples during aging. The data obtained from samples aged at 39° C are given in Table I. These are representative of results obtained at other temperatures,

TABLE I

ALKALINITY DECLINE OF NEOPRENE LATEX AT 39° C

Titer to pH 10.5 (meq/100 g)

Time (weeks)	Type 571					Type 842-A					Type 601-A				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
0	0.4	1.2	2.2	3.2	4.0	1.2	1.8	2.3	3.3	4.3	1.1	2.4	3.4	4.3	5.2
1	0.4	1.1	2.0	3.0	3.9	1.1	1.7	2.1	3.1	4.2	1.0	2.4	3.3	4.3	5.2
3	0.1	0.8	1.7	2.7	3.6	0.8	1.5	2.0	3.0	4.0	0.8	2.2	3.1	4.2	5.0
7	0.0	0.6	1.6	2.5	3.5	0.7	1.3	1.9	2.8	3.9	0.5	1.8	3.1	3.8	4.7
14		0.2	1.2	2.2	2.8	0.3	0.8	1.3	2.1	3.3	0.2	1.5	2.6	3.5	4.4
17		0.0	0.8	1.8	2.5		0.6	0.9	1.9	3.0		1.0	2.2	3.2	4.0
22			0.5	1.6	2.1		0.2	0.7	1.6	2.7		1.0	2.1	3.0	3.6
27			0.2	1.2	2.0		0.0	0.2	1.4	2.3		0.5	1.7	2.4	3.2
32			0.1	0.9	1.7			0.0	1.2	2.1		0.3	1.2	2.2	3.0

pH

	Type 571					Type 842-A					Type 601-A				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
0	11.3	11.9	12.3	12.5	12.6	11.8	12.2	12.3	12.5	12.6	12.0	12.4	12.6	12.7	12.7
1	11.3	11.9	12.3	12.5	12.6	11.8	12.2	12.3	12.5	12.6	12.0	12.4	12.5	12.7	12.7
3	10.9	11.7	12.2	12.4	12.5	11.6	12.1	12.2	12.4	12.5	11.9	12.3	12.4	12.6	12.6
7	10.5	11.4	12.1	12.4	12.5	11.2	12.0	12.1	12.4	12.5	11.5	12.2	12.4	12.5	12.6
14	10.2	10.9	12.0	12.2	12.4	10.8	11.7	11.9	12.2	12.4	10.7	11.7	12.0	12.3	12.6
17	10.1	10.5	11.5	12.0	12.1	10.3	11.1	11.5	12.0	12.2	10.4	11.7	11.9	12.2	12.3
22	10.0	10.4	11.2	11.8	12.0	10.4	10.9	11.3	11.9	12.0	10.2	11.7	11.8	12.1	12.2
27	Coag	10.2	10.9	11.7	11.9	10.3	10.5	10.8	11.8	11.9	10.0	11.4	11.8	12.0	12.1
32		Coag	10.6	11.5	11.7	Coag	10.4	10.5	11.6	11.8	9.7	10.9	11.6	11.9	12.0

except for differences in rate. The data show that, as the alkali level increases, differences of alkali content are not so readily discernible from pH measurements as from direct titer measurements, because pH measurements are a logarithmic function. This is brought out clearly in the table, where it will be noted that some samples of the same latex which show little or no difference in pH vary widely in alkali content, when determined by direct titer measurement. In addition, although not readily evident from the pH data, the titer data show that the rate of free alkali consumption is practically constant throughout the aging period. This is illustrated in Figure 1, where the results obtained with the Type 571 latex samples are plotted. The data indicate that these latexes had already passed through the initial aging period of changing rate of chlorine liberation, as discussed by Andersen and Arnold[1], who have shown that the rate of chlorine evolution from the polymer in Neoprene latex becomes con-

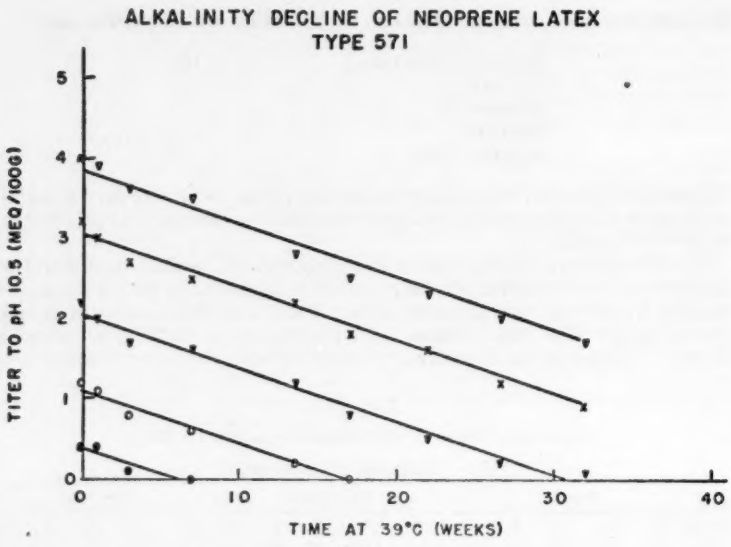


FIG. 1.

stant after a relatively short initial period. It should be noted that this rate is independent of the alkali content.

The effect of free alkali content on the storage life of raw and compounded latex at 50° and 70° C is shown by the data in Table II. Storage life was de-

TABLE II

EFFECT OF ALKALINE RESERVE ON STORAGE LIFE OF NEOPRENE LATEX

	Original titer to pH 10.5 (meq/100 g)	Coagulation time (days)			
		Raw		Compounded	
		50° C	70° C	50° C	70° C
Type 571					
Sample No. 1	0.4	33	4	33	3
Sample No. 2	1.2	100	7	66	4
Sample No. 3	2.2	125	14	134	9
Sample No. 4	3.2	138	21	145	9
Sample No. 5	4.0	150	23	164	9
Type 842-A					
Sample No. 1	1.2	74	7	39	4
Sample No. 2	1.8	101	7	94	7
Sample No. 3	2.3	111	9	94	7
Sample No. 4	3.3	145	10	117	8
Sample No. 5	4.3	180	10	126	9
Type 601-A					
Sample No. 1	1.1	135	11	47	7
Sample No. 2	2.4	185	22	70	8
Sample No. 3	3.4	194	23	105	9
Sample No. 4	4.3	197	30	145	9
Sample No. 5	5.2	197	30	171	9

fined as the time required for the sample to coagulate completely. These data, illustrated in Figure 2 for the Type 571 latex samples, show that higher alkali content increased markedly the life of both raw and compounded latex. While it is recognized that the most reliable prediction of storage life is obtained only by making aging tests at the temperature to be encountered, some indication of the improvement effected by increased alkali content can be obtained from the work done by Andersen and Arnold[1]. They have found, with Type 571 latex samples aged out of contact with air, that one day at 50° C is equivalent to about a week or more at room temperature. Using this comparison, it appears that increasing the titer of a latex from 1 to 3 would increase its storage life at room temperature from about one year to more than two years.

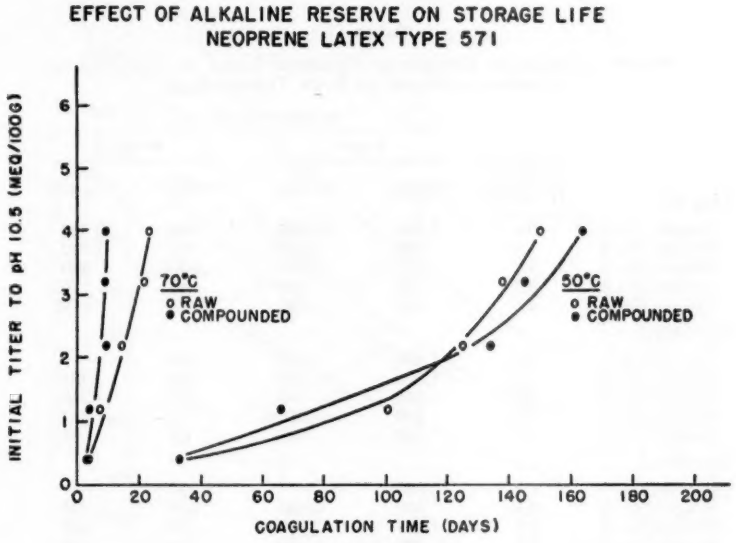


FIG. 2.

Viscosity changes are often considered indicative of the stability characteristics of latex compounds. To study the effect of alkali content on the usability of the compounds prepared in this work, the viscosity was measured periodically with a Brookfield L-4 viscometer. Two speeds were used, 6 and 60 rpm. The No. 1 spindle was used for all cases except those in which the reading was off the scale for either speed. In such instances a smaller spindle was substituted and readings were made with it at both 6 and 60 rpm. The data in Table III show the original viscosities and the viscosities after aging for five months at room temperature as a function of the initial titer. They show that increasing amounts of free sodium hydroxide decrease the original viscosity and extend the useful life of compounds by reducing very much the viscosity increase which takes place during aging. This is graphically illustrated in Figure 3 for the Type 571 latex samples; the data are plotted on semilogarithmic coordinates because of their exponential character.

Having established the important influence of the free alkali level on the aging and usability of Neoprene latex compounds, a study was made of the effect of free alkali content on the curing speed and physical properties of films prepared from such compounds. Films were dipped from the compounds by the American Anode process, utilizing a five-minute dwell with a coagulant of calcium chloride-calcium nitrate in acetone and methanol[3]. The films were leached for two hours in Permutit water at room temperature, dried overnight, and then for four hours at 70° C, and subsequently cured at 141.5° C. Stress-strain properties of the films, shown in Table IV, indicate that there were only slight differences among films from compounds prepared from the same latex at different alkali levels. Other work with compounds containing several of the common Neoprene-latex curing additives has indicated that the same is

TABLE III

EFFECT OF ALKALINE RESERVE OF NEOPRENE LATEX ON VISCOSITY OF COMPOUNDS STORED AT ROOM TEMPERATURE

		Brookfield viscosity (cps)			
		6 rpm		60 rpm	
	Original titer to pH 10.5 (meq/100 g)	Original	After 5 months	Original	After 5 months
Type 571					
Sample No. 1	0.4	1,600	16,000	560	5,400
Sample No. 2	1.2	520	6,160	250	1,240
Sample No. 3	2.2	320	1,200	150	360
Sample No. 4	3.2	160	440	84	176
Sample No. 5	4.0	116	240	43	116
Type 842-A					
Sample No. 1	1.2	1,460	2,420	520	—
Sample No. 2	1.8	1,040	1,420	320	488
Sample No. 3	2.3	640	940	262	360
Sample No. 4	3.3	240	380	96	163
Sample No. 5	4.3	108	240	62	90
Type 601-A					
Sample No. 1	1.1	12,800	—	3,200	—
Sample No. 2	2.4	260	4,800	158	1,216
Sample No. 3	3.4	200	1,080	122	480
Sample No. 4	4.3	200	400	114	248
Sample No. 5	5.2	220	200	118	132

true of more complex compounds. It should be noted, however, that, as shown by Livingston and Walsh[7], the increased stability of Neoprene latex as a result of increased alkali content results in a decreased rate of deposition in coagulating dip processes. This fact may limit the extent to which one should stabilize his Neoprene latex compounds by this method.

While this work has shown that increasing amounts of alkali improve the processing and storage life of Neoprene latexes and their compounds, it has not indicated that there is an upper limit to the amount of alkali which should be used, except in those few instances where film deposition rate may be very critical. Andersen and Arnold[1] have shown that the addition of excessive alkali to raw latex can cause it to pass through a region of incipient instability during aging even sooner than the region would have been encountered had less alkali or no alkali at all been added. The amount of alkali which will cause

this condition depends on both the chloride ion and the positive ion concentra. tions in the latex, which in turn depend on the age of the latex and its history. Because of the effect of these variables on the tolerable upper caustic level and because of the possibility of incipient instability when these large amounts of caustic are used, no attempt was made to explore the high caustic regions. In some isolated experiments, where latexes of high titer were used, compounding problems have been encountered at titer levels of six to eight. Difficulty from

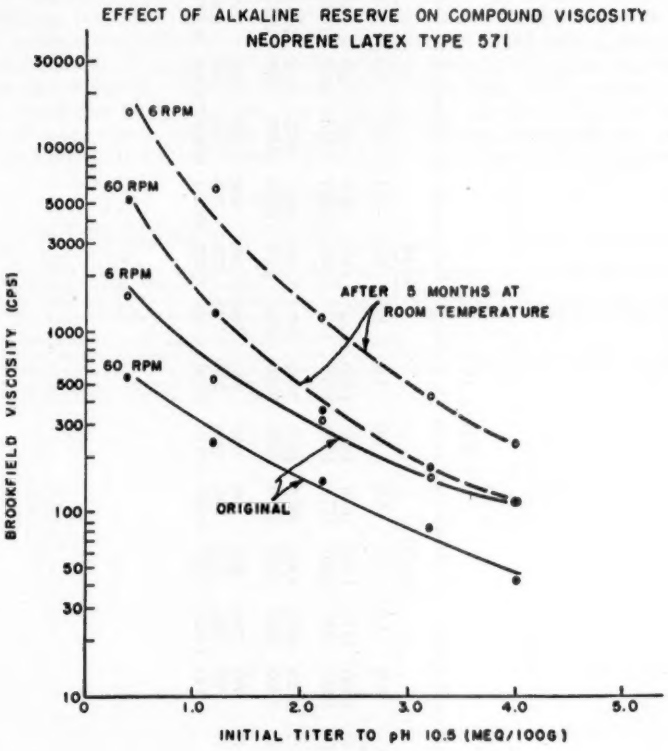


FIG. 3.

excessive alkali has not been noted at titers in the region of 4. Since such titers should be adequate for most purposes, there would seem to be little reason for employing higher ones.

Adjustment of the titer of raw latex as a means of obtaining improved stability of both it and its compounds is simple and straightforward and should be entirely adequate for raw latex. However, it is possible that it may be inadequate for those compounds containing ingredients capable of consuming some of the sodium hydroxide. In such cases it is probable that best results could be obtained by adjustment of the titer of the compound itself. The practicabil-

TABLE IV

EFFECT OF ALKALINE RESERVE OF NEOPRENE LATEX ON PHYSICAL PROPERTIES OF FILMS FROM COMPOUNDS

	Type 571					Type 842-A					Type 601-A				
Titer to pH 10.5 (meq/100 g)	0.4	1.2	2.2	3.2	4.0	1.2	1.8	2.3	3.3	4.3	1.1	2.4	3.4	4.3	5.2
Stress at 600% Elongation (psi)															
Cure: 30 minutes at 141.5° C	1000	1175	1150	1050	1025	1150	1325	1250	1075	925	925	750	775	775	775
60 minutes at 141.5° C	1300	1325	1650	1575	1500	1275	1525	1525	1500	1575	1225	1025	1250	1100	1000
Tensile Strength (psi)															
Cure: 30 minutes at 141.5° C	2775	2975	3200	3275	3275	2800	2875	3050	2825	3075	2750	2675	2375	2775	2375
60 minutes at 141.5° C	3200	3500	4000	3800	3950	3200	3500	3400	3700	3750	3300	2925	3000	2825	2800
Elongation at Break (%)															
Cure: 30 minutes at 141.5° C	800	790	880	890	910	770	780	780	800	900	900	950	930	930	900
60 minutes at 141.5° C	770	800	760	780	800	760	770	770	780	780	800	800	810	800	820
Average Thickness* (inches)	0.030	0.025	0.022	0.020	0.019	0.026	0.025	0.023	0.020	0.019	0.026	0.024	0.023	0.022	0.021

* Five-minute dwell time.

ity of this procedure is not known, but further laboratory work planned on the titer method of compounding Neoprene latex will include investigation of this variation.

SUMMARY

The practical importance of free alkali content on the processing and storage life of Neoprene latexes, both raw and compounded, is demonstrated. It is shown that titer measurements are more sensitive than pH measurements for establishing the alkali level of Neoprene latex, that increasing amounts of alkali increase markedly the life of both raw and compounded latexes, that increasing amounts of alkali decrease the original viscosity of compounds and reduce very much the viscosity increase which takes place during aging but, that, within the ranges checked, the alkali content has little effect on the physical properties of films. A procedure for measuring accurately and adjusting easily the free alkali content of raw latex to a desired level is suggested.

REFERENCES

[1] Andersen and Arnold, *Ind. Eng. Chem.* **45**, 2727 (1953).
[2] Maynard, J. T., and Mochel, W. E., "The Structure of Neoprene. VII. Infrared Analysis of Configuration", in press.
[3] Cook, G. S., and Fitch, J. C., Report No. 52–3, "Neoprene Dipped Goods", E. I. du Pont de Nemours & Company, Rubber Chemicals Division, Dec. 1952.
[4] Emulphor ON-870, a polyoxyethylated fatty alcohol sold by General Dyestuff Corporation, is usually used. Other nonionic stabilizers or stabilizers of the condensed naphthalenesodium sulfonate type have been used.
[5] Subsequent use of the word *titer* in this paper has this meaning.
[6] Five per cent sodium hydroxide has proved satisfactory for use in the laboratory in most instances. Because of the possibility of flocculation, higher concentrations can seldom be used; lower concentrations may be advisable when agitation is inadequate.
[7] Livingston and Walsh, *Ind. Eng. Chem.* **38**, 1262 (1946).

ZINC SOAP FORMATION AND THE GELLING OF LATEX *

J. L. M. NEWNHAM

RESEARCH CENTRE, DUNLOP RUBBER CO., LTD., FORT DUNLOP, ERDINGTON, BIRMINGHAM, ENGLAND

INTRODUCTION

Wren[1] found that the solubility of zinc oxide in 1.3 per cent ammonia and in latex serum is increased by mineral and amino acids and by fatty acids of low molecular weight, and also that zinc ammine ions form insoluble compounds with soaps. Recently Kraay and van den Tempel[2] showed that zinc soap formation is necessary for the gelling of latex with zinc compounds, and suggested that the mechanism is a reaction of zinc ions in solution in the latex serum with adsorbed fatty acid soaps.

Zinc oxide dissolves in aqueous ammonia solutions to form complex zinc ammine ions. The formation of these complex ions has been studied by a number of investigators, who have mostly found that the ammine formation stops at a tetrammine complex. Bjerrum[3] concluded that zinc generally forms a tetrammine ion, and that the number of complex bound ammonia molecules increases in a smooth formation curve with free ammonia concentration up to a maximum of four, the four ions having a range of coexistence. Change of temperature or of ammonium salt concentration only displaces the formation curve as a whole.

Latex may be gelled at room temperature by ammonium salts, zinc oxide and soap alone at a pH value between 10 and 9 within a few minutes, and the gelling pH of latex gelled with, say, sodium silicofluoride and zinc oxide is usually between pH 9 and 8. Taking the solubility of zinc ions to be:

$$[Z_n{}^{++}] = 4 \times 10^{-18}/[OH']^2 \text{ at } 25° \qquad (1)$$

as given by Kolthoff and Kameda[4], the concentration of soluble zinc as zinc ions in latex serum can be calculated to be 4×10^{-6} g.-ion per liter at pH 8 and 4×10^{-10} g.-ion per liter at pH 10. Analytical results show that a normal centrifuged latex may contain about 4.5 grams of soap per liter of latex, of average molecular weight 350. This amount of soap needs 1.7×10^{-2} g.-ion of zinc per liter of serum for complete precipitation, neglecting any soap added in compounding. It is clear, therefore, that the small concentration of zinc ions available in these regions of pH is not sufficient in itself to take any significant part in the gelling. Further, it has been demonstrated[5] that zinc oxide has no gelling action on latex at high pH, except in the presence of ammonia. In view of this, it is likely that complex zinc ammine ions mainly react with soaps at these pH values. That is:

$$Zn(NH_3)_n{}^{++} + 2(R.COO') \rightleftharpoons (R.COO)_2Zn + nNH_3 \qquad (2)$$

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 29, No. 3, pages 160–172, June 1953.

where n, the average number of complex bound molecules coordinated to each metal ion, depends on the free (*i.e.*, uncombined) ammonia concentration and, therefore, on pH:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH' \quad (3)$$

The extent of zinc soap formation in a latex serum containing given amounts of available zinc, ammonium salts and ammonia is, therefore, largely dependent on the concentration and reactivity of the complex zinc ammines formed in solution. The reactivity of zinc ammines towards soaps would be expected to be greater with low values of n, since with a smaller number of bound ammonia molecules the complex ions have a higher mobility and charge density. The zinc ion is more chemically reactive than the complex ions, but, as has been shown, is present in only small concentration at the pH of gelling. Hence variables affecting the amount and composition of the complexes present in a latex serum, for example, pH and temperature, determine the zinc soap formed and thus gelling of the latex.

This paper describes a study which has been made of the influence of some of the variables affecting zinc soap formation, and deductions which have been made concerning the gelling of latex.

EXPERIMENTAL

Solubility of zinc oxide.—The solubility of zinc oxide in a given sample of latex serum is known to depend on the ammonium salts present and on the free ammonia content of the solution. The latter factor will change where gelling involves the neutralization of the ammonia, *e.g.*, with sodium silicofluoride. It is important, therefore, to know how the solubility of zinc oxide varies with change of pH during the course of gelling.

The solubility of zinc oxide was determined in an ammonia/ammonium sulfate solution and in latex serum at different ammonia concentrations. The serum was obtained by creaming a centrifuged latex of 30 per cent total solids

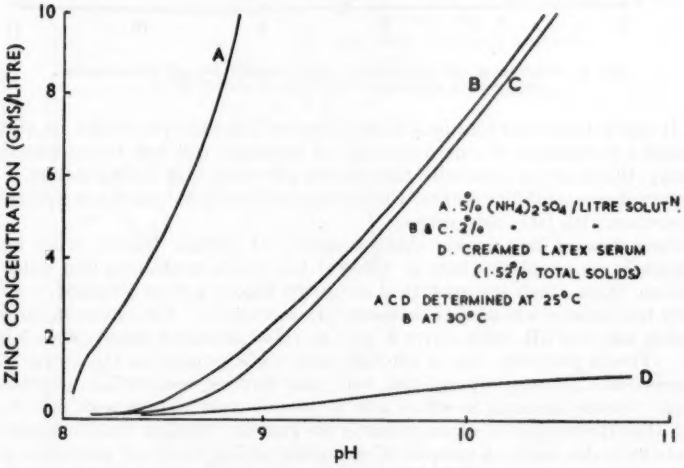


FIG. 1.—Solubility of zinc oxide in ammonium salt/ammonia solutions and in latex serum.

with ammonium alginate. The results shown as a function of pH are given in Figure 1. The amount of zinc oxide taken into solution depended on the ammonium salt concentration and pH, and fell to almost zero solubility at pH 8, corresponding to the decrease in ammonia concentration and thus in zinc ammine ion formation. The solubility increased with temperature. Figure 2 shows the variation of solubility of zinc oxide in two samples of sera, similar except for initial ammonia content, at equilibrium pH values reached with different additions of sodium silicofluoride in the presence of excess zinc oxide. In Figure 2 the pH value was lowered below 8 and minimum solubility was again found at about this pH. The increase in solubility with fall of pH to values below that corresponding to the minimum solubility is mainly due to zinc ions.

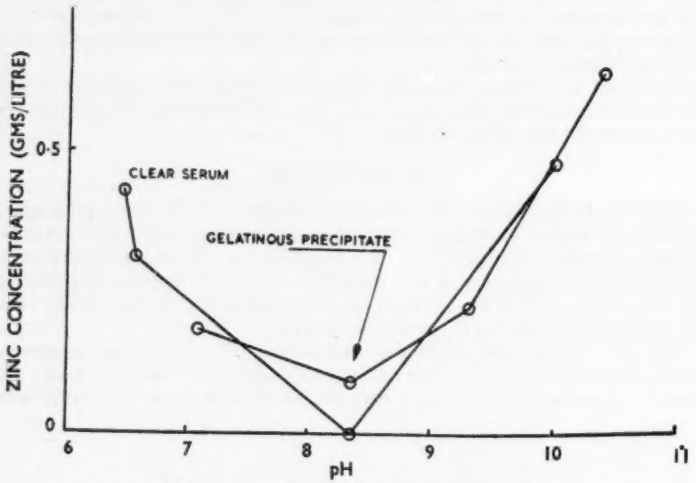


FIG. 2.—Solubility of zinc oxide in latex serum at equilibrium pH values reached with varying additions of sodium silicofluoride at 25° C.

It was noticed that solutions of zinc ammine ions left open to the air, slowly formed a precipitate of zinc hydroxide as ammonia was lost by evaporation. It may, therefore, be concluded that, as the pH value falls during gelling, a reduction of zinc solubility occurs, with consequent precipitation of zinc hydroxide or reaction with fatty acid soaps.

Formation of zinc soaps.—Measurements of surface tension were made (Figure 3) on samples of sera at different pH values containing zinc oxide in solution, from which the analytical results of Figure 2 were obtained. A Du Nouy tensiometer was used to measure surface tension. The minimum surface tension was at a pH value above 9, and its value increased rapidly with fall of pH. This is probably due to the fact that soaps present in the serum were progressively removed by reaction with zinc forming non-surface active zinc soaps. Hence the form in which zinc is present must change with fall of pH such that the formation of zinc soap is facilitated. Surface tension measurements were also made on samples of serum containing dissolved zinc oxide with progressive lowering of pH by the addition of acid (Figure 4). Graph 1 illus-

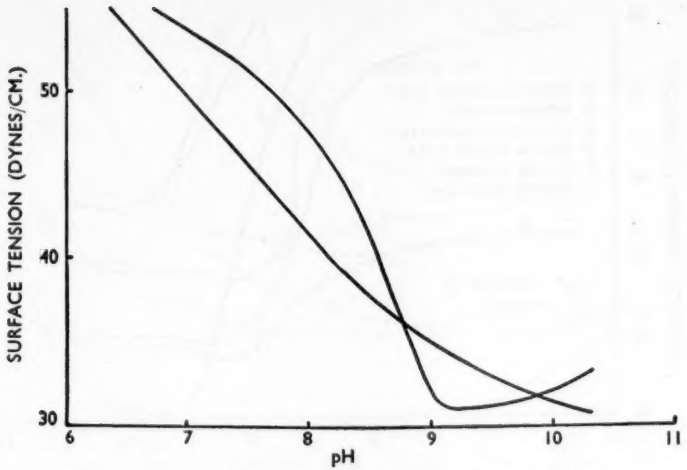


FIG. 3.—Surface tension of serum containing zinc oxide in solution (pH lowered by sodium silicofluoride additions).

strates the effect of change of pH on the surface tension of serum from a normal centrifuged latex, in the absence of zinc oxide. The minimum surface tension from pH 8 to 7 corresponds to the formation of surface-active acid soap[6]. In graph 2 with zinc in solution, the minimum is now given at pH 0.4, followed by a rise in surface tension, indicating precipitation of zinc soap with fall of pH. Graph 3 is for a serum obtained from a latex to which 1.5 per cent oleic acid was added before centrifuging. The minimum surface tension here is at pH 9.6 and the rise, with lowering of pH, less sharp.

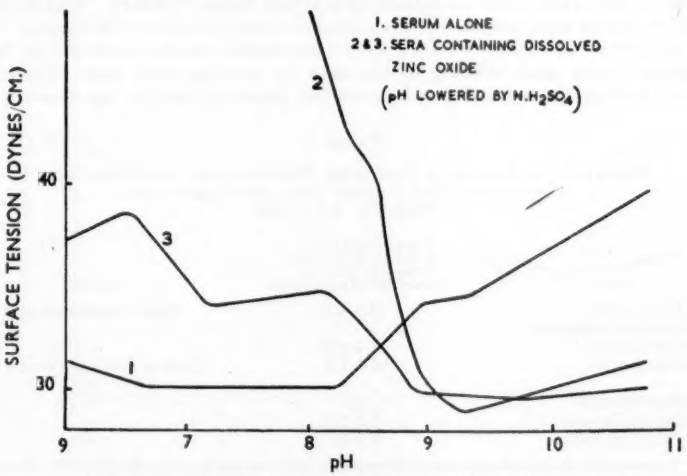


FIG. 4.—Surface tension/pH variations of latex sera containing dissolved zinc oxide.

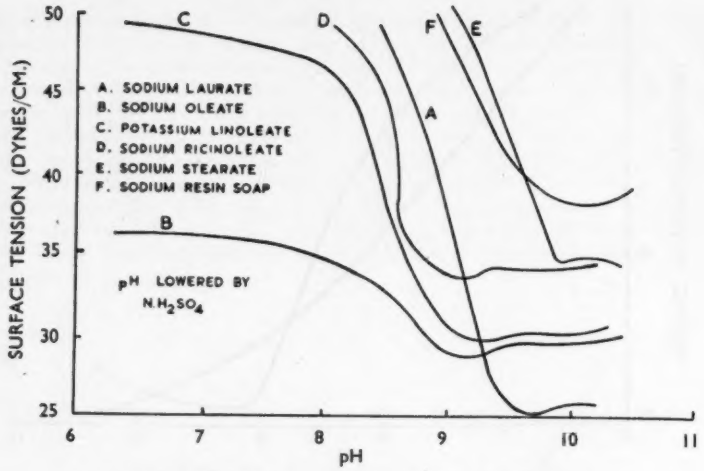


FIG. 5.—Surface tension/pH graphs for solutions of zinc ammine ions and soaps.

Investigation of zinc soap formation with a number of different soaps was then carried out (Figure 5). Solutions were made up containing 1.5 per cent sulfuric acid, 0.2 per cent of zinc oxide, 2.4 per cent ammonium hydroxide, and approximately 1 per cent of various soaps. The amount of zinc in solution was in excess of the minimum necessary to precipitate the whole of the soap used. Normal sulfuric acid was then added to the mixed solutions and change of surface tension with pH recorded. The solutions were clear initially at pH 10.3, except with resin soap, progressive precipitation of zinc soap was then observed with each of the soaps used, as acid was added (Table 1). The surface tension values are a measure of the unreacted soap present. The upward rise of the curves in Figure 5 at pH values below that of the minimum surface tension, occurs after removal of the soap by reaction with zinc. Figure 6 shows surface tension/pH graphs obtained similarly, but in the absence of

TABLE 1

RELATIVE pH VALUES OF ZINC SOAP PRECIPITATION FROM SOLUTIONS CONTAINING ZINC AMMINE IONS AND SOAPS WHEN TITRATED WITH ACID

Soap	Temperature 22° C pH Range of zinc soap formation observed (Formation of precipitate)	Remarks
Castor oil soap (Sodium ricinoleate)	9.0–8.9	Some cloudiness at 9.4
Sodium laurate	9.4–8.9	—
Sodium oleate	10.4–8.6	Bulk of zinc soap formed at 8.6
Sodium stearate	9.9	—
Potassium linoleate	9.2–9.0	—
*Sodium resin soap	9.4–9.1	—

* Sodium resin soap is the sodium salt of disproportionated rosin acids, sold as Dresinate 731 (Hercules Powder Co.).

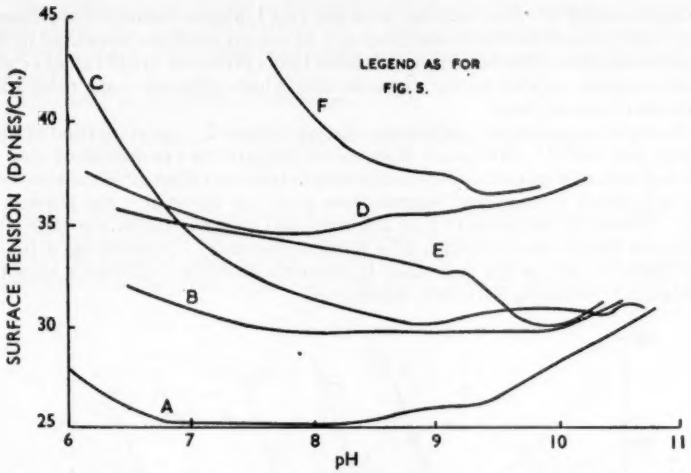


FIG. 6.—Surface tension/pH graphs for solutions containing soaps, ammonium sulfate and ammonia. Solutions as given for Figure 5 except that no ZnO was present.

soluble zinc. The minima now given are in each case at lower pH values than in the presence of zinc and are due to surface active acid soap being formed.

Since the zinc ion concentration, according to Equation 1, is small at the pH values recorded for the formation of zinc soaps in Table 1, the species resonsible for interaction with soaps must be lower complex zinc ammine ions. With fall of pH the concentration of free ammonia is reduced with correspond-

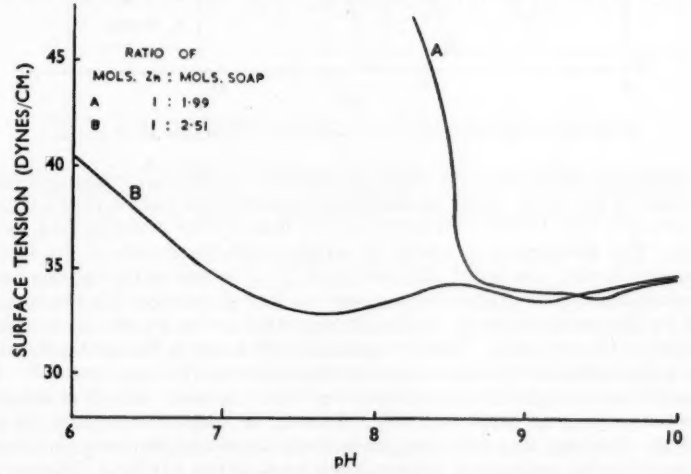


FIG. 7.—Surface tension/pH graphs for solutions of zinc ammine ions and castor oil soap at different soap concentrations.

ing reduction of n. The complex ammine ions therefore become more chemically reactive and zinc soaps are formed. As similar solutions were used in the experiments with different soaps, it follows that differences in pH values of zinc soap formation depend on the aptitude with which different soaps react with particular ammine ions.

In similar experiments with castor oil soap (Figure 7), the proportion of soap to zinc was varied. With soap in excess of the ratio two molecules of soap to one molecule of zinc as the pH fell, the surface tension values after the zinc soap was completely precipitated became those given for the soap in the absence of zinc. These results indicate that the soap and zinc reacted in the ratio 2:1, corresponding to the formation of a normal zinc soap. However no attempt was made to analyze the zinc soap in order to determine whether a complex precipitate containing ammonia was formed.

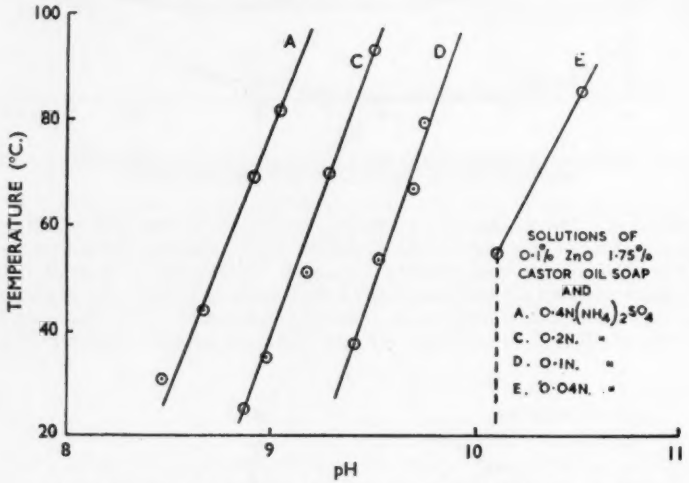


FIG. 8.—Variation in temperature of zinc soap formation with initial pH of solution.

Formation of zinc soap with rise of temperature.—Solutions containing known amounts of zinc oxide, castor oil soap, ammonium sulfate, and varying amounts of ammonia were heated with gentle stirring in test tubes immersed in a water bath. The temperature at which the solutions just became turbid due to the zinc soap formed was noted (Figures 8 and 9). On raising the solution temperature higher, more and more zinc soap was formed; initially this was emulsified by the unreacted soap, but finally separated out as an oily layer at the bottom of the test tube. Thus for example, with graph A, Figure 9, a solution becoming turbid at 60° gave a complete separation into two layers at 80°. An approximate straight line relationship was found between the pH of solution and temperature of initial turbidity. Increase of temperature raised the pH level at which zinc soap formation commenced, other conditions being constant. Increase in ammonium salt concentration lowered this pH level, whereas increase of zinc concentration had the converse effect.

The surface tension and turbidity results show that zinc soap formation takes place over a range of falling pH or rising temperature; this can be explained by change of equilibria in which lower and more active zinc complexes are formed.

The essential equilibria involved are:

$$Zn(NH_3)_n^{++} + 2(R.COO') \rightleftharpoons (R.COO)_2Zn + nNH_3 \quad (2)$$

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH' \quad (3)$$

More ammonium salt present at constant pH or hydroxyl ion concentration necessitates more free ammonia being formed for equilibrium, hence n is increased; the complex ammines are, therefore, less reactive, and less zinc soap is formed. Similarly for higher pH values at constant ammonium salt con-

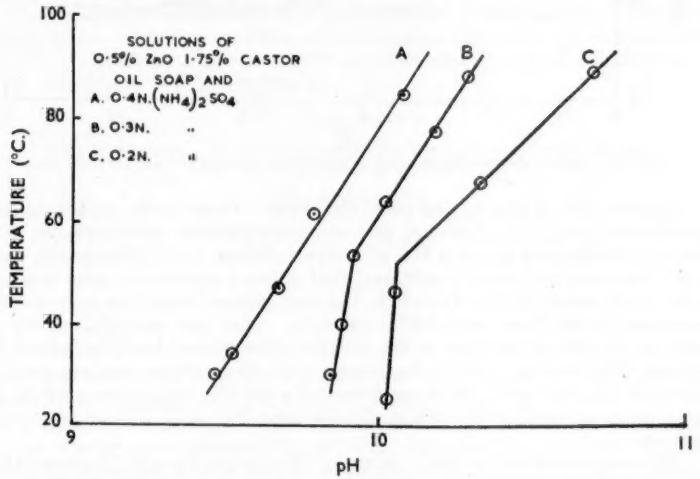


FIG. 9.—Variation in temperature of zinc soap formation with initial pH of solution.

centration, more ammonia needed to raise the pH causes corresponding increase of free ammonia concentration. The effect of variation of zinc concentration is explained by a decrease in the value of n increasing the reactivity of the ammine species.

This mechanism allows an explanation of the gelling effect of ammonium salts and zinc oxide. Gelling takes place when sufficient zinc soap has been formed to cause inversion of phase. The graphs of Figures 8 and 9 show that generally an extrapolation of the pH of zinc soap formation can be made from room temperature to higher temperatures. It may, therefore, be concluded that the same mechanism is responsible for zinc gelling, whether caused by raised temperature, lowered pH, or by a combination of both factors. Lowering the pH may be caused by additional acid forming agents or by the suppression of ionization of the ammonia by the ammonium salt added. In the latter case the time of gelling is governed partly by the rate of dissolution of zinc oxide in the serum.

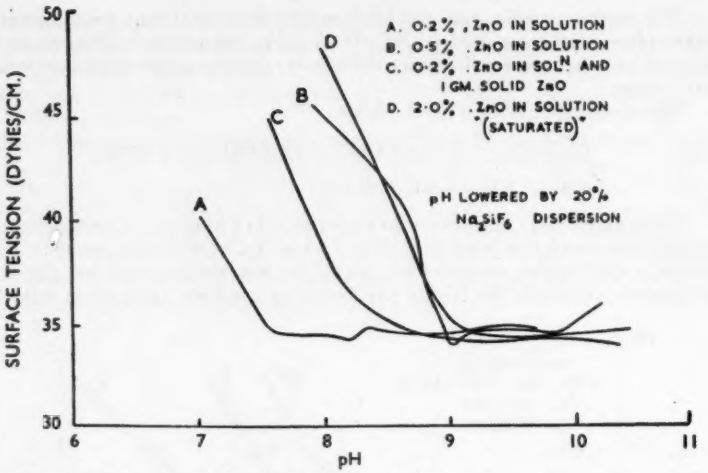


FIG. 10.—Surface tension/pH graphs for solutions of zinc ammine ions and castor oil soap.

Sequestration of zinc by sodium silicofluoride.—Some of the surface tension experiments previously described gave anomalous results when repeated using sodium silicofluoride to lower the pH value. It was found (Figure 10), using 1 per cent castor oil soap in solution, that unless a quantity of zinc was used much in excess of that equivalent to the soap present, all of the soap was not converted to zinc soap with fall of pH to 8. This may be explained by adsorption of zinc ammine ions on the colloidal silica formed by hydrolysis of the sodium silicofluoride. Smith[7] has shown that zinc ammine ions are strongly adsorbed on silica gel. Since an excess of solid zinc oxide was used in the previous experiments with sodium silicofluoride (Figure 5), this effect was not noticed.

Zinc soap formation in latex.—Murphy, Madge and Pounder[8] reported that, on adding zinc oxide to an ammonia-preserved latex containing castor oil soap and then gelling with sodium silicofluoride, the pH of gelling was raised above that in the absence of soap and tended to a value of 8.9 This pH corresponds to the point at which most zinc soap was formed in the experiments of Table 1. A similar result is shown by gelling pH figures given in Table 2. Zinc oxide in

TABLE 2

EFFECT OF ZINC OXIDE ON GELLING pH OF AMMONIA-PRESERVED LATEX IN PRESENCE OF CASTOR OIL SOAP

(Ammonia content 0.25 per cent)

Soap (% on dry rubber)	Zinc oxide (% on dry rubber)	Gelling pH	Remarks
0.67	—	7.5	—
0.67	3.2	8.6	Sodium silicofluoride added immediately after zinc oxide
0.67	3.2	8.8	Sodium silicofluoride added 10 min. after zinc oxide

the presence of soap raised the gelling pH from 7.5 to 8.6. Longer standing in presence of zinc oxide allowed more time for solution to take place, giving more complete precipitation of soap with lowering of pH, and the gelling pH was then raised to 8.8.

Other gelling pH values were carried out with different soaps, but no general correlation with the relative zinc soap precipitation figures was obtained, possibly due to the adsorption of zinc ammine ions by colloidal silica obscuring the formation of zinc soap, or possibly due to variations in the degree to which different soaps are adsorbed at the rubber-water interface, causing differences in their availability for reaction with zinc ammine ions and in the effect of the zinc soaps when formed.

Gel strength data obtained by the method described by Madge[9] illustrates the practical importance of zinc soap formation in giving maximum strength to latex gels (Table 3).

Castor oil soap and zinc oxide added separately to the latex gave little or no change of gel strength, but when added together raised the gel strength considerably. It is clear, therefore, that zinc soap formation is an essential factor in the attainment of a firm strong gel.

TABLE 3

GEL STRENGTH. (FORCE NECESSARY TO SNAP SMALL CLYINDER OF GEL OF STANDARD CROSS-SECTION)

(Temperature 21°)

Zinc oxide (% on dry rubber)	Castor oil soap (% on dry rubber)	pH of gel at test	Gel strength (Average figures)
—	—	7.8	187 gm.
—	0.3	7.7	190 gm.
1.6	—	7.7	260 gm.
1.6	0.3	7.8	400 gm.

Formation of zinc soap is of considerable importance in latex processes, especially with regard to the stability of sensitized mixes. The pH at which zinc soap is formed will vary with the composition of the mix, but with castor oil soap was generally between 9.4 and 8.6. This may be one reason why the Z.O.T. test does not always give a correlation with the KOH no.[10]. Since the Z.O.T. test is carried out at an ammonia content of 0.05 per cent, which approximates closely to pH 9.0, variations of viscosity will occur, due to slight changes of ammonia content, which greatly affect the formation of zinc soap. The knowledge gained of the factors which control the formation of zinc soap should aid in formulating a test of zinc activity in which these factors are more closely controlled. Further work is now being done on this problem.

Conclusions.—The solubility of zinc oxide in the serum of an ammonia-preserved latex has been found to vary more or less linearly with pH over the range of 10.5 to 8.0, and to fall to a minimum solubility near the latter pH value. Increase of temperature and ammonium salt concentration raises the zinc solubility. No attempt was made to determine the variation with different ammonium salts, but the work of Cassagne[11] indicates that this is also an important factor.

Fall of pH of a latex over the region 10.5 to 8.0 reduces the solubility of zinc oxide, and precipitation of zinc hydroxide occurs. If soaps are present in solution, progressive precipitation of zinc soap over a range of falling pH takes place, as shown by surface tension measurements. Kraay and van den Tempel

have shown that zinc soap formation is an essential factor in the gelling of latex, and it is now suggested that formation of zinc soap takes place during the gelling of latex by acid-forming gelling agents. However, in the case of sodium silicofluoride, zinc ammine ions are adsorbed by the colloidal silica formed, lessening the effect of zinc in reacting with soap during gelling.

Zinc soap formation is an imporant factor in the attainment of maximum gel strength.

Zinc soap formation took place over a range of temperature, as shown by the turbidity developed in solutions of zinc ammine ions and soaps on heating. The conditions of zinc soap formations varied both with ammonium salt and zinc concentrations. Increase of the last or decrease of the zinc concentration raised the temperature and lowered the pH of the range at which the zinc and soap reacted.

The following mechanism is proposed for the formation of zinc soap from zinc ammine ions and soaps. It is known that zinc forms a range of ammines which exist in equilibrium, their composition depending on the concentration of free or uncombined ammonia. Increase of temperature or fall of pH of a particular solution containing ammonia, ammonium salt, and zinc reduce the average number of ammonia molecules coordinated to each zinc ion. The lower zinc ammines thus formed, and in the limit zinc ions, are more chemically reactive due to their greater charge density and higher mobility, and reaction with soap occurs. Further work remains to be done on the physicochemical factors involved in order to verify the above theories. It is suggested that an improved test for zinc activity might now be developed in which the zinc soap formation is more closely controlled.

SUMMARY

The gelling effect of zinc oxide on ammoniated latex is known to be due to the formation of zinc soaps. The object of the present work was to investigate the formation of zinc soaps under varying conditions in order to elucidate the gelling mechanism more clearly. The main variables affecting the zinc ammine ion formation in an ammonia solution containing given amounts of ammonium salts and soluble zinc are pH and temperature. Falling pH or rising temperature favor formation of the more chemically reactive lower zinc ammine ions, and give rise to the formation of zinc soaps if soaps are present.

It is suggested that zinc soap formation in the serum of ammoniated latex and the consequent gelling of the latex depend on the presence of specific zinc ammine ions.

ACKNOWLEDGMENTS

Appreciation is expressed to the Dunlop Rubber Co., Ltd., for permission to present this paper and to various colleagues, in particular to E. W. Madge for helpful discussion and suggestions.

REFERENCES

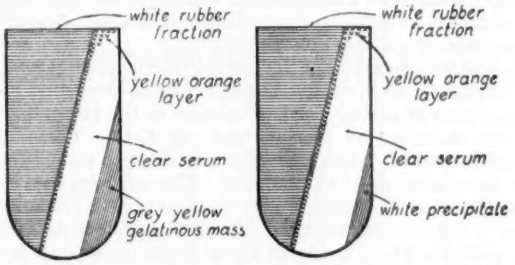
[1] Wren, *Trans. Inst. Rubber Ind.* **18**, 91 (1942).
[2] Kraay and van den Tempel, *Trans. Inst. Rubber Ind.* **28**, 144 (1952).
[3] Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haass and Son, **1941**.
[4] Kolthoff and Kameda, *J. Am. Chem. Soc.* **53**, 832 (1931).
[5] Panich, Kal'yanova, and Voyutskil, *Kolloid. Zhur.* **12**, 50 (1950).
[6] Powney and Addison, *Trans. Faraday Soc.* **34**, 356 (1938).
[7] Smith, *J. Phys. Chem.* **43**, 637 (1939).
[8] Murphy, Madge, and Pounder, *Proc. Rubber Tech. Conf.* (London), **1948**, p. 303.
[9] Madge, *Trans. Inst. Rubber Ind.* **28**, 207 (1952).
[10] Murphy, *Ind. Eng. Chem.* **44**, 756 (1952).
[11] Cassagne, "La Thermosensibilité du Latex d'Hevea", Paris, Hermann & Cie. **1951**.

FRACTIONS FROM HEVEA BRASILIENSIS LATEX CENTRIFUGED AT 59,000 g *

A. S. Cook and B. C. Sekhar

Chemical Division, Rubber Research Institute of Malaya, Kuala Lumpur, Malaya

Homans and van Gils[1] have separated fresh latex, by centrifuging at 2,000 r.p.m. (*ca.* 1,000 g.) into two fractions, white and yellow, both consisting mainly of rubber particles and serum. They also reported the discovery of another discrete phase in fresh latex, which they called lutoids, and which were found mainly in the yellow fraction. Huret[2] has described the separation of ammoniated latex at 400,000 g. into a white fraction, a yellow layer, and clear serum. We have obtained four distinct fractions on centrifuging fresh latex at 20,000 r.p.m. (59,000 g.), and these have not previously been described, although McColm[3] has reported on the sludge obtained at 40,000 r.p.m.



a *Fresh latex* b *Latex containing 0.5% NH_3*

Fig. 1.

Latex was collected from a field of mixed clonal seedlings at the Rubber Research Institute of Malaya Experiment Station and cooled in an ice-water mixture within an hour of tapping the first tree. Part of the latex was weighed into Lustroid (celluloid) tubes fitted with air tight caps and spun at 59,000 g. in a refrigerated vacuum centrifuge[4] at 5° C for three-quarters of an hour. Another portion of the latex was ammoniated to 0.5 per cent NH_3 by weight, using a 20 per cent solution. Part of this latex was centrifuged with the fresh latex and part after 24 hours. Figure 1 represents diagrammatically the separations obtained.

The fractions were separated by puncturing the tube at the top and the bottom of the serum fraction and allowing the serum to run out. The top portion of the serum was mixed with part of the yellow orange layer and some rubber particles. Both the top and bottom fractions were very viscous and did not flow. They were readily obtained by cutting open the Lustroid tube.

* Reprinted from the *Journal of the Rubber Research Institute of Malaya*, Vol. 14, pages 163–167, September 1953.

The fractions and a sample of the fresh latex were dried in air at 70° C and analyzed. Results are given in Table I.

It was difficult to separate part of the serum from the yellow orange layer; hence, the exact amounts of each fraction, except the bottom fraction, were not obtained accurately. Nevertheless, an approximate distribution of the various components among the fractions is given in Table II.

From the fresh latex, the top white fraction was a very thick cream of rubber particles, comprising roughly 60 per cent of the whole latex and containing 70–80 per cent solids. Most of this fraction could be redispersed in water.

The yellow orange layer was obtained mixed with serum and rubber particles. Under the microscope, considerable numbers of spherical yellow particles were seen, either singly or in small clusters. These were very similar to the description given by Frey-Wyssling[5] of the yellow globules which he observed in ammoniated latex.

The serum was clear and slightly brown, comprising about 25 per cent of the whole latex and containing 7 per cent solids. It was somewhat viscous, frothed readily, and appeared to contain most of the proteins, phosphorus, potassium, copper, ash, and part of the magnesium present in the whole latex.

The grayish yellow bottom fraction comprised 12–15 per cent of the whole latex and contained 12 per cent solids. It was very compact, and on standing in air, it slowly darkened to a dark brown, finally becoming black. It did not coagulate, but remained as a thick paste, which did not appear to dissolve in water. In ammonia solution, it slowly dissolved to give a brown solution and a white precipitate, which was crystalline.

Microscopical investigations of the bottom fraction, before and after mixing with water, ammonia, and sodium citrate solutions, showed it to consist of a tightly packed mass of gellike "islands" similar to the lutoid islands found in fresh latex and described by Homans and van Gils[1]. These islands had a particulate structure and, when ammonia solution was added, many particles in Brownian movement could be observed. The particles could be rubber or lutoid globules, such as are found in very fresh latex or in latex which has been collected into sodium citrate solution. After dissolving in ammonia for a few days, many particles which appeared to be rubber were seen and also a few yellow Frey-Wyssling particles. This fraction contained most of the magnesium and, taking the nitrogen as being protein, it consisted of about 40 per cent alcohol extractables, about 30 per cent protein, 17 per cent ash and 15 per cent rubber. The presence of rubber could be attributed to rubber particles being trapped in the lutoid agglomerates.

Ammonia in the latex appeared to dissolve or disperse the lutoid fraction, giving in its place a white precipitate. The effects of the ammonia took place rapidly, as will be seen by comparing the analyses of fractions from the ammoniated latex (1) centrifuged almost immediately, and (2) after 24 hours. The bottom fraction from (1) was slightly larger than that from (2), indicating incomplete dispersion. The top white fraction and the orange yellow layer from the ammoniated latex were similar to those from the fresh latex.

More serum was obtained from the ammoniated latex; about 40 per cent of the whole latex containing 9 per cent solids. It was cloudy and, compared with the serum from the fresh latex, it contained more nitrogen and potassium, about the same proportion of copper, less phosphorus, and practically no magnesium.

The white precipitate at the bottom of the tube was only about 2 per cent of the whole latex, and contained 32 per cent solids. Compared with the lutoid

TABLE I

ANALYSES OF FRACTIONS

Determination	Latex fraction	Fresh latex, stored in iced water and centrifuged 1 hour after collection	Latex containing 0.5% NH_3 centrifuged 1 hour after collection	Latex containing 0.5% NH_3 centrifuged 24 hours after collection	Fresh latex, not centrifuged
Dry rubber content [%-wt.]	Whole latex	—	—	—	44.24
Total solids [%-wt.]	Whole latex	—	—	—	47.65
Nitrogen [%-wt.]	Dried rubber	0.21	0.21	0.25	0.57
	Dried serum	2.29	4.23	5.78	
	Dried bottom fraction	5.23	4.54	3.94	
Magnesium [%-wt.]	Dried rubber	0.01	0.01	0.01	0.07
	Dried serum	0.28	0.01	0.01	
	Dried bottom fraction	1.25	7.82	8.00	
Phosphorus [%-wt.]	Dried rubber	0.04	0.04	0.04	0.13
	Dried serum	0.67	0.54	0.63	
	Dried bottom fraction	2.06	8.00	9.62	
Potassium [%-wt.]	Dried rubber	0.04	0.08	0.05	0.42
	Dried serum	4.72	5.75	5.04	
	Dried bottom fraction	3.13	1.34	1.24	
Copper [%-wt.]	Dried rubber	0.00017	0.00021	0.00036	0.00040
	Dried serum	0.00594	0.00341	—	
	Dried bottom fraction	0.00439	0.00500	—	
Ash [%-wt.]	Dried rubber	0.28	0.35	0.26	1.16
	Dried serum	11.20	9.23	—	
	Dried bottom fraction	17.11	29.47	39.96	
Rubber hydrocarbon [%-wt.]	Dried rubber	96.3	—	96.6	90.6
	Dried bottom fraction	14.9	—	—	
Alcohol extract [%-wt.]	Dried rubber	1.88	—	2.24	6.54
	Dried bottom fraction	42.15	—	—	
Total acid value [mg. KOH/100 g. t.s.]	Dried rubber	34	—	62	301
	Dried bottom fraction	3,983	—	—	

TABLE II

APPROXIMATE DISTRIBUTION OF COMPONENTS AMONG THE FRACTIONS
(%-wt. of whole latex)

Determination	Fresh latex centrifuged after 1 hour			0.5% NH_3 latex centrifuged after 1 hour			0.5% NH_3 latex centrifuged after 24 hours		
	Rubber	Serum	Bottom fraction	Rubber	Serum	Bottom fraction	Rubber	Serum	Bottom fraction
Nitrogen	34	35	31	28	64	8	37	58	5
Magnesium	16	30	54	11	0.5	88.5	12	0.5	87.5
Phosphorus	34	54	12	19	29	52	24	26	50
Potassium	7	74	19	10	87	3	12	85	3
Copper	20	62	18	31	58	11	—	—	—
Ash	14	54	32	20	58	22	—	—	—

fraction from fresh latex, it contained more magnesium and phosphorus and less nitrogen, potassium, and copper. Under the microscope, it was seen to consist almost entirely of star-shaped crystals. This precipitate is likely to be the same as that which has previously been described in the sludge from ammoniated latex[3], and is probably a magnesium phosphate.

Conclusions from these observations are that four fractions can be separated from fresh latex by centrifuging at 59,000 g: a thick cream of rubber particles; a layer of orange yellow Frey-Wyssling globules below the rubber; clear serum; and a gelatinous grayish yellow lutoid fraction at the bottom of the tube. Ammonia in the latex appeared to dissolve or disperse the lutoid fraction, forming an insoluble magnesium phosphate.

ACKNOWLEDGMENT

We are indebted to J. E. Morris and his assistants for the analyses.

REFERENCES

[1] Homans and van Gils, *Proc. 2nd Rubber Technol. Conf. London*, 1948, p. 292.
[2] Huret, *Rev. gén. caoutchouc* **25**, 124 (1948).
[3] McColm, *Ind. Eng. Chem.* **32**, 439 (1940).
[4] Spinco Ultracentrifuge, Model L.
[5] Frey-Wyssling, *Arch. Rubbercultuur* **13**, 392 (1929).

TENSILE PROPERTIES OF FILMS FROM LOW-TEMPERATURE GR-S LATEX *

R. W. BROWN, W. E. MESSER, AND L. H. HOWLAND

Naugatuck Chemical Division, United States Rubber Co., Naugatuck, Connecticut

The tensile properties of evaporated films from synthetic rubber latex are of interest from both theoretical and practical considerations. From the theoretical point of view, film tensiles give a measure of the inherent properties of polymers which have not been subjected to processes of flocculation and mastication. Practically, film tensiles may be used to predict the approximate tensile properties of latex-derived polymer in some technical applications, although results will not be directly comparable because of the different conditions employed. Natural-rubber films have been the object of many investigations and their excellent tensile properties are well known[1]. It is also well established that GR-S latex containing predominant amounts of butadiene and polymerized at high temperatures (about 40°C) gives films with tensile strengths on the order of 10 per cent of those from natural rubber latex[2]. This value can be increased to about one-half that of natural rubber by increasing the amount of styrene in the copolymer to around 50 per cent, but only with the sacrifice of much of the rubberlike quality of the polymer, particularly at subfreezing temperatures[3].

With the development of low-temperature GR-S polymerization, new latexes became available, and early work on low-solids latex which had been concentrated by creaming indicated that a very marked improvement in film tensiles was achieved by lowering the temperature of polymerization[4]. Film tensiles of 2500 to 3300 pounds per square inch were obtained on three latexes prepared at 5°C, and values in excess of 4000 pounds per square inch were obtained from one latex prepared at −18°C. These results were six to ten times as great as are normally obtained from latex of the same monomer ratio polymerized at high temperatures. Following this work, low temperature (10°C) recipes for high-solids latexes were developed and put into commercial production[5]. Although these latexes gave much improved properties in some applications[6], considerable difficulty has been encountered in reproducing the high film tensiles obtained previously on concentrates of low-solids latexes[7].

In view of these facts, it was decided to set up a program for latex film testing in this laboratory with the object of determining the factors which have caused the difficulties in reproducing the early work on low-temperature latexes and testing new latexes as they become available. This paper describes the results of this program to date.

EXPERIMENTAL WORK

The general experimental technique employed has been described by Peaker[8].

The latexes, normally at 50 to 60 per cent solids, were compounded in 400-cc. beakers with gentle mechanical agitation. Sufficient latex was used to give

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 6, pages 1322–1329, June 1953. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Buffalo, N. Y., October 29–31, 1952.

100 grams of latex solids, and all compounding was done on this basis. The agitator had a low pitch, so arranged as to draw latex from the bottom of the beaker in order to avoid creating a vortex. Compounding ingredients were added as solutions or ball-milled dispersions, and the mixture was allowed to agitate for several minutes before the thickener was added. In some early work air bubbles were removed by adding a few drops of a benzene dispersion of silicone defoamer and reducing the pressure to the point that the latex boiled at room temperature. This procedure was abandoned when it was found that the defoamer caused depressions (fish eyes) in the films. With careful agitation little trouble with air bubbles was experienced. Very viscous samples such as X-635 at over 60 per cent solids were diluted to 50 per cent and allowed to stand for a day or two before use. The latex was not matured after compounding.

The compounded thickened latex was strained through 150-mesh stainless steel screens directly onto 10×18 inch glass plates and spread into films 6 inches wide and 0.03 inch thick with a stainless steel spreader bar. Films were normally allowed to dry overnight at room temperature and humidity, although in some cases films laid in the morning were removed from the plates in the late afternoon. In general, the sooner the films were removed the more easily they were separated from the plates. No trouble with cracking was experienced as long as sufficient thickener was present. The dried films were dusted with talc, stripped from the plates, and dusted on the reverse side. They were then cut into three sections and cured for 15, 30, and 60 minutes at 105°C in a circulating air oven. Normally, curing was carried out on the day following that on which the films were laid. The cured films were stored in the open in the laboratory. When a sufficient number had been accumulated, tensile strips were died out by hand with a standard $\frac{1}{8}$×1 inch dumbbell die and gauged for thickness. The strips were normally 0.009 to 0.015 inch thick, depending on the per cent solids of the compounded latex. The prepared samples were stored overnight in a constant temperature room (77°F, approximately 50 per cent relative humidity) before testing. Tensiling was conducted on a standard Scott tester of 10 pounds capacity at a jaw separation of 20 inches per minute.

Some films, particularly those containing rosin soap, stuck tightly to the glass plates. It was found that coating the plates with a very thin film of polyvinylbutyral (0.25 per cent in *sec*-amyl alcohol) gave good release with no measurable effect on film tensiles. This technique was employed on all samples containing rosin soaps.

All the films contained 3.0 parts of zinc oxide and 2.0 parts of sulfur added as a single ball-milled dispersion (these amounts are not critical). When casein was employed as a thickener, 2.0 parts per 100 parts of latex solids were used, added as a 10 per cent solution in dilute ammonia. If necessary, more water was added to give the desired viscosity. Other thickeners were not used in measured amounts, but were added in sufficient quantity to give the desired latex viscosity.

METHOD OF REPORTING DATA

In general, three samples were tested from each cure and the average of the two highest values, rounded off to the nearest 100 pounds per square inch, was reported as the tensile for that cure. This procedure differs somewhat from that of the American Society for Testing Materials, in which the median value is reported. It is, however, felt to be justified for this type of work where small flaws will initiate tears and cause very low apparent tensiles. Latex-deposited

films are notoriously subject to these flaws, and the precision of tensile testing does not approach that of press-cured stocks. These difficulties are aggravated in many of these synthetic rubber films, which possess high tensile strength and low tear resistance. Many of the results in the following tables show this lack of precision. The conclusions which have been drawn generally are based on considerably more data than are presented here.

Elongations were also calculated from the average of the two strips having the highest tensiles. Elongations are more reproducible than tensiles, for, because of the low modulus of these unreinforced stocks, little stress is developed until the last few per cent elongation before break. Consequently, examples are frequently found where the tensiles of two duplicate samples differ by 50 per cent or more of the higher value while elongations differ by no more than 2 or 3 per cent.

POTASSIUM OLEATE-EMULSIFIED LATEXES

X-635 Latex

Accelerator Variations.—At the time this project was initiated, X-635 latex was in commercial production at the Naugatuck plant and was, therefore, selected as the standard for preliminary investigation. More recently this latex has been largely superseded by improved formulations, but because its study laid the foundation for much of the later work it is discussed first. X-635 is a 60+% solids latex of 70/30 butadiene-styrene charge ratio, polymerized at low temperature to a Mooney viscosity of 70–100 ML-4. A drum

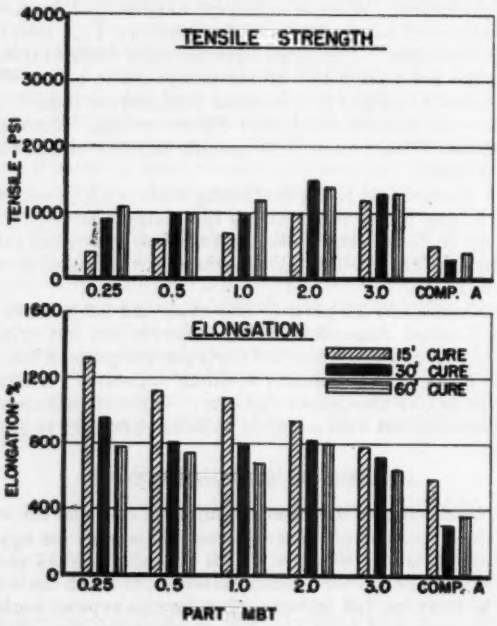


Fig. 1.—Effect of varying mercaptobenzothiazole on X-635 film tensiles.

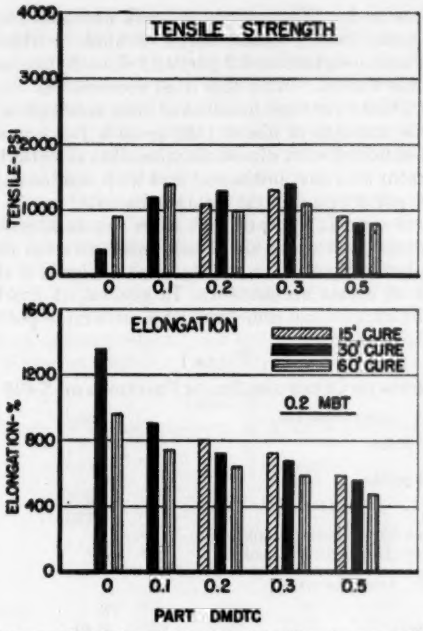


FIG. 2.—Effect of varying dimethylammonium dimethyldithiocarbamate on X-635 film tensiles.

of this material from the plant production was reserved for the laboratory in order to give a large homogeneous sample for study.

The first work was carried out using an accelerator system composed of 1.5 parts of zinc mercaptobenzothiazole and 0.5 part of zinc dibutyldithiocarbamate per hundred parts of latex solids. This is a mixture which has been recommended[8] and frequently used for latexes polymerized at high temperatures. Accelerator, zinc oxide, and sulfur were added as a single ball-milled dispersion designated Composite A. Film tensiles and elongations were both uniformly low at all cure times, indicating that the samples were badly overcured. Several series of films were then prepared with varying levels of acceleration in an attempt to find a more useful system. In order to take advantage of the somewhat less powerful accelerating action of water-soluble salts as well as to facilitate the addition and dispersion of small and varying amounts of accelerator, the dimethylamine salts of mercaptobenzothiazole (MBT) and dimethylammonium dimethyldithiocarbamate (DMDTC) were selected for study. Mercaptobenzothiazole was added on the basis of the mercaptobenzothiazole present, while the dithiocarbamate was added on the basis of the total dimethylamine salt.

Figure 1 shows the film tensiles of a series of latexes compounded with varying amounts of mercaptobenzothiazole compared with those of a film compounded with Composite A. It is apparent that considerably higher tensiles were obtained with the mercaptobenzothiazole, the highest figure being 1500 pounds per square inch, somewhat more than three times that of the

control with Composite A. Elongations at break were also improved. Figure 2 shows tensile results from a similar series of films in which the mercaptobenzothiazole was held constant at 0.2 part and dimethylammonium dimethyldithiocarbamate was varied. With this dual acceleration, amounts of dithiocarbamate from 0.1 to 0.3 part per hundred of latex solids gave good cures, with an optimum tensile strength of about 1400 pounds per square inch. Similar results have been obtained with dimethylammonium dimethyldithiocarbamate as the sole accelerator (0.3 part optimum) and with combinations of mercaptobenzothiazole and potassium dibutyl dithiocarbamate.

From the above data it appears that these low-temperature latexes cure extremely rapidly and that optimum tensile properties are obtained at much lower accelerator levels than are normally used. Figure 2 shows clearly the deleterious effects of excess accelerator. In general, it has been found that 0.3 part of dimethylammonium dimethyldithiocarbamate per hundred of latex

TABLE I

COMPARISON OF CREAM AND SERUM FRACTIONS OF X-635 LATEX

A. Latex Properties	Cream	Serum
% of total latex	10	90
% solids	82	46
% of total solids	16	84
pH	9.8	10.4
% screens	0.195	0.002
Viscosity at 45% solids (Brookfield)	15	17
Filterability, grams at 45% solids	Nil[a]	300+
B. Latex Properties [b]		
ML-4	78	105
% ash, total	0.10	0.13
% ash, H_2O-soluble	0.10	0.12
% soap	0.005	Nil
% fatty acid[c]	1.12	4.08
% bound styrene	25.2	25.2
% gel	40	48
Swelling index	64	56
Dilute solution viscosity	1.06	1.14

[a] Filterability of total latex approximately 1 gram.
[b] Determined on polymer obtained by salt-acid coagulation.
[c] Present as soap in latex.

solids is a satisfactory accelerator level for latexes containing approximately 70 per cent butadiene.

From these results, along with many others which have been obtained in the course of the work, it appears that, in general, X-635 latex from plant production gives films by the present technique with a tensile of about 1400 pounds per square inch at optimum cure, although occasional specimens give values up to 2000 pounds per square inch. This is a considerable improvement over tensiles obtained previously from this latex, but still not so good as those reported earlier or those obtained from some other latexes now being produced.

Cream Removal.—As it is produced in the plant, X-635 latex contains a considerable amount of material of very large particle size, which comes to the surface as a heavy cream. Rough calculations of the minimum particle diameter of this cream from the rate of sedimentation on mild centrifuging showed that most of the material was over 100,000 A (0.01 mm.) in particle diameter. Particles of this size probably should be classed as precoagulum rather than as cream.

Table I shows the results of some physical and chemical tests on cream and serum fractions of the latex which had been allowed to separate by standing. The most striking difference between the two fractions is in the amount of soap present. The low Mooney viscosity of the cream fraction appears anomalous, but otherwise the results are normal. The high filterability of the serum fraction indicates that practically all of the large particles have been removed. This test, which indicates the amount of microscopic coagulum, is essentially similar to the strainability test of Brass and Slovin[9].

Because the calculations of particle size mentioned above showed that the cream or prefloc was in the range which could be studied microscopically, photomicrographs were made of several of the latexes from which films were being prepared. Figure 3 shows some of these photomicrographs. It is apparent that much of the "cream" is of extremely large particle size compared to the latex particles (1000 to 2000 A. diameter), thus confirming the calculations from rates of sedimentation. All the photomicrographs were taken on latex diluted to 5 per cent solids.

TABLE II

EFFECT OF CREAM REMOVAL ON X-635 FILM TENSILES

Treatment	Cured at 105°C (min.)	—	Centrifuged	Centrifuged and filtered	—	Centrifuged	Centrifuged and filtered
Lignin		—	—	—	2.5	2.5	2.5
DMDTC		0.3	0.3	0.3	0.75	0.75	0.75
Thickener		Casein			Alginate		
Tensile (lb./sq. inch)	15	800	800	500	1400	1700	1400
	30	1100	1600	1600	1700	1900	2400
	60	1300	1800	2100	1600	2000	2400
Elongation (%)	15	900	1060	1260	740	820	840
	30	800	840	920	680	630	700
	60	730	740	740	580	600	580

As preliminary tests indicated that the tensiles of films from the serum fraction were somewhat higher than those of the normal latex, a more careful study was carried out. The cream layer gave films with very poor tensiles (ca. 600 pounds per square inch).

A quantity of X-635 latex was diluted to 50 per cent solids and centrifuged at 2000 r.p.m. for 30 minutes. This treatment compacted the cream layer to such an extent that it could be punctured and the underlying latex poured off without disturbing the solid upper layer. A portion of the centrifuged latex was set aside in a large separatory funnel for several days to allow any residual large particles to rise to the surface, and was then drained slowly from the funnel through a felt filter. About 90 per cent of the latex ran through the felt rapidly, but the last 10 per cent would not filter, even through a clean felt, indicating that some large particles were still present in the centrifuged latex.

The three samples (untreated, centrifuged, and filtered) were compounded with (*a*) 0.3 part of dimethylammonium dimethyldithiocarbamate with casein as thickener, and (*b*) 0.75 part of dimethylammonium dimethyldithiocarbamate and 2.5 parts of lignin (Indulin A, West Virginia Pulp and Paper Co.) with an alginate thickener. Lignin has been found (see below) to improve the reproducibility of film testing. Photomicrographs were also prepared from the three latex samples at 5 per cent solids (Figure 3). Table II shows film tensile results

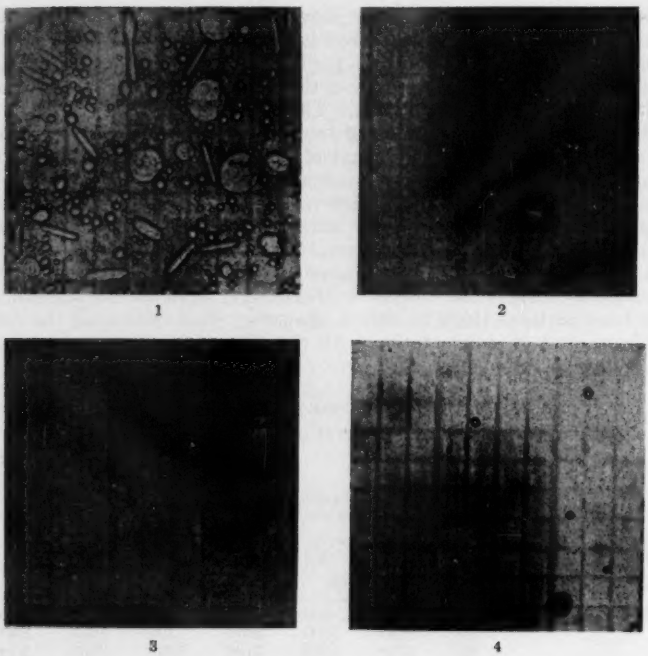


FIG. 3.—Low temperature high-solids latexes.
Grating space equals 5×10^4 A.

1. X-635
2. Centrifuged X-635
3. Centrifuged filtered X-635
4. High ML-4 X-635

of the three samples. It is evident that an increase of about 400 pounds per square inch in optimum tensile has been brought about by removal of the cream fraction by centrifuging. Filtration of the centrifuged latex gave further improvement in tensile, although the photomicrographs show relatively little change. From this work it appears that the true tensiles of films from X-635 latex from which the large particles have been removed are upwards of 2000 pounds per square inch.

Effect of Shortstop on Cure Rate.—Most of the low-temperature high-solids latexes now in production are shortstopped with water-soluble dithiocarbamate salts. Although no appreciable acceleration of cure is normally found in dry polymers, it seemed likely that there would be an effect in latex compounding where the polymer is not flocculated and washed. A series of bottle runs was prepared in an unmodified X-635 formula and shortstopped with (*a*) 0.25 part per hundred of monomers of potassium dimethyldithiocarbamate (KDMDTC), (*b*) 0.25 part of potassium monoethyldithiocarbamate (KMEDTC), and (*c*) 0.2 part of hydroquinone plus 0.04 part of hydrogen peroxide. The latexes were stripped, concentrated, and compounded with 1.5 part of mercaptobenzothia-

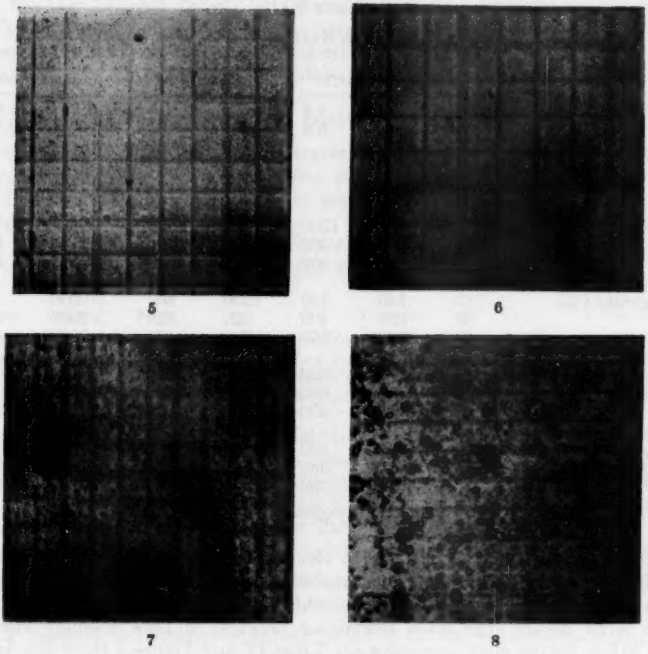


FIG. 3.—*Continued*

5. Centrifuged high ML-4 X-635
6. Centrifuged filtered high ML-4 X-635
7. J-5000-C
8. X-684

zole and also with 1.5 parts of mercaptobenzothiazole plus 0.4 part of potassium dibutyldithiocarbamate (KDBDTC).

Table III shows that potassium dimethyldithiocarbamate added as shortstop remained very active as an accelerator of cure. The monosubstituted dithiocarbamate gave weaker activation, while the latex shortstopped with hydroquinone gave films which did not cure up at all in 60 minutes with mercaptobenzothiazole acceleration. From these results it is evident that the dithiocarbamate added as shortstop must be considered in the compounding of low-temperature GR-S latex.

OTHER X-635 TYPE LATEXES.—In the development of new high-solids latexes, the pilot plant has prepared a number of variations of the X-635 formula which have been evaluated in films. J-4828 (150 ML-4, 60 per cent conversion) and J-4862 (150 ML-4, 80 per cent conversion) in particular were studied extensively in order to determine whether high Mooney viscosity and lower conversion have any effect on film tensile properties. Both of these latexes gave optimum film tensiles of about 2000 pounds per square inch, *i.e.*, better than X-635 as it is produced, but no better than centrifuged X-635. Neither of these latexes had any appreciable amount of cream, and their film tensiles were not improved by centrifuging. It appears that in the range of 60

TABLE III

EFFECT OF SHORTSTOP ON CURE RATE OF X-635 TYPE LATEX FILMS

Shortstop		KDMDTC		KMEDTC		Hydroquinone + H_2O_2	
MBT		1.5	1.5	1.5	1.5	1.5	1.5
KDBDTC		—	0.4	—	0.4	—	0.4
	Cured at 105°C (min.)						
Tensile (lb./sq. inch)	15	2100	1200	900	1900	Nil	1300
	30	1600	400	800	1700	Nil	600
	60	1200	900	1000	900	Nil	800
Elongation (%)	15	740	540	1230	660	>2000	700
	30	650	400	920	620	>2000	440
	60	620	500	880	460	>2000	410
Aged tensile[a] (lb./sq. inch)	15	2400	600	1900	2300	500	1800
	30	1100	800	1500	2500	400	700
	60	1600	400	2100	1200	1700	800
Elongation (%) Aged[a]	15	560	330	790	540	>2000	460
	30	470	380	740	520	>2000	320
	60	480	280	740	420	1130	340

[a] Vulcanised film aged 24 hours at 75°C in circulating air oven.

to 80 per cent conversion and 100 to 150 ML-4 neither percentage conversion nor Mooney viscosity has any measurable effect on film tensile properties.

Another latex of this general type which has met with interest from some users is an X-635 type latex containing polymer of high Mooney viscosity (170 ML-4, 70 per cent conversion). Table IV and Figure 3 show film tensile data and photomicrographs of this latex as it was obtained and after removal of material of large particle size. Centrifuging and filtration were carried out as described above for X-635. In this case, also, a considerable increase in film tensile was brought about by filtering the centrifuged latex, although the photomicrographs show little change. The best tensiles were slightly better than those of X-635. Although there is much less cream in the new product than in X-635, it has an equivalent effect on lowering the film tensiles. Apparently relatively few particles of microscopic coagulum cause inhomogeneities which lead to low tensiles. The high tensile films from filtered X-635 and the

TABLE IV

EFFECT OF CREAM REMOVAL FROM HIGH MOONEY VISCOSITY X-635 TYPE LATEX ON FILM TENSILES

(0.3 DMDTC accelerator, casein thickener)

Treatment	Cured at 105°C, (min.)	—	Centrifuged	Centrifuged and filtered
Tensile (lb./sq. inch)	15	1100	1800	2000
	30	1400	1800	2100
	60	1600	1800	2500
Elongation (%)	15	750	780	760
	30	680	690	700
	60	660	660	660

high Mooney viscosity variety both showed considerably greater variation from specimen to specimen than J-5000-C type latexes of equivalent tensile values, suggesting that the all-fatty-acid films are more sensitive to small imperfections than those containing rosin-type acids.

MIXED ROSIN–FATTY ACID EMULSIFIED LATEXES

J-5000-C Latex.—During the course of the work with X-635 and related latexes described above, a new series of low-temperature high-solids latexes based on mixed rosin acid-fatty acid soap emulsification was made available.

Table V

Disproportionated Tall Oil Emulsified High-Solids Latexes

Number	ML-4	Emulsifier	Monomer ratio
J-4993	128	Neo-Fat K-242+K oleate	70/30
J-5000-A	134	Neo-Fat K-242+K oleate	70/30
J-5000-C	166	Neo-Fat K-242+K oleate	70/30
X-635	70–100	K oleate	70/30

Most of these have used the potassium soap of a disproportionated tall oil fraction containing about 60 per cent rosin acid as the emulsifier. Preliminary testing of film from these latexes gave much higher tensiles than those which had been obtained from X-635. Table V summarizes some features of three of these latexes compared to X-635 and Table VI gives film tensile results. It is evident that all three of these latexes give film tensiles on the order of 2500 to 3000 pounds per square inch.

Table VI

Film Tensiles of Disproportionated Tall Oil Emulsified High-Solids Latex
(Casein thickener, mixed MBT-DTC accelerator)

Latex		J-4993	J-5000-A[a]	J-5000-C[a]	J-5000-C[b]	J-5000-C[c]	X-635
	Cured at 105°C. (min.)						
Tensile (lb./sq. inch)	15	2700	..	..	2900	2800	1500
	30	3000	2500	3500	3300	3400	1500
	60	1600	2400	2500	3000	3200	1400
Elongation (%)	15	840	..	..	780	710	800
	30	760	740	710	660	680	740
	60	690	660	620	600	620	710

[a] Uncured film stuck to plates. Cured on plates.
[b] Uncured film removed from glass with difficulty.
[c] Film laid on varnished glass surface.

As these materials appeared to be definite improvements over X-635 both as to film tensiles and for some commercial applications, it was decided to shift considerable development work from X-635 type to one of them. J-5000-C, variations of which have now gone into production as X-683 (50 per cent solids) and X-684 (60 per cent solids), was selected for more thorough study. Figure 4 shows the results of compounding J-5000-C latex with varying levels of dimethylammonium dimethyldithiocarbamate with casein as thickener. It is apparent that, as was the case with oleate emulsified latexes, about 0.3 part of dimethylammonium dimethyldithiocarbamate gives optimum results, larger

amounts of accelerator causing rapid decrease in tensile. Since previous work with X-635 latex had shown that the dithiocarbamate salt used in shortstopping contributes to curing, a control was prepared in this series with no added accelerator. Appreciable curing took place due to acceleration by the shortstop. Also included in Figure 4 are tensile results from a film compounded with Composite A. As with X-635, this high level of accelerator reduced the film tensiles to little more than a third of the optimum.

Similar film tensile results have been obtained from this latex with mercaptobenzothiazole and mixtures of mercaptobenzothiazole and dimethylammonium dimethyldithiocarbamate as accelerator. All three accelerator systems give

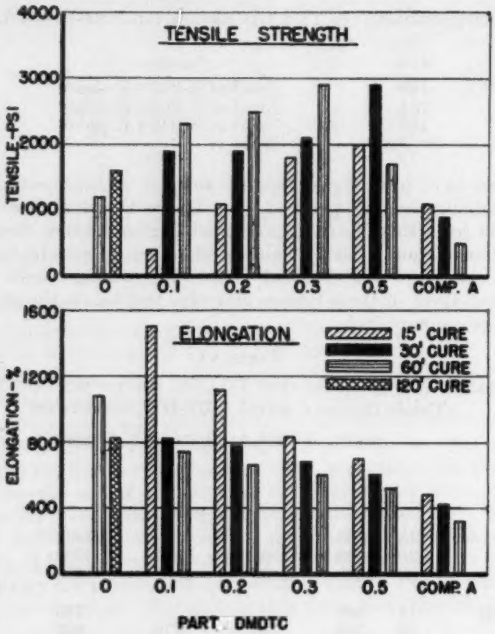


FIG. 4.—Effect of varying dimethylammonium dimethyldithiocarbamate on J-5000-C film tensiles.

about the same optimum film tensiles, although results with the dithiocarbamate appear to be somewhat more reproducible. J-5000-C latex contained relatively little microscopic coagulum (Figure 3) and centrifuging did not improve the film tensiles.

Effect of Cure Retarders.—In an investigation of several potential reinforcing agents in latex films, it was found that small amounts of lignin as the ammonium or sodium salt brought about an apparent increase in film tensile. Further study of this phenomenon showed that tensiles obtained with lignin seldom exceeded the best values obtained without it, but that the high values were much more reproducible, particularly over a wider range of accelerator levels and curing times. Somewhat similar results have been obtained in the

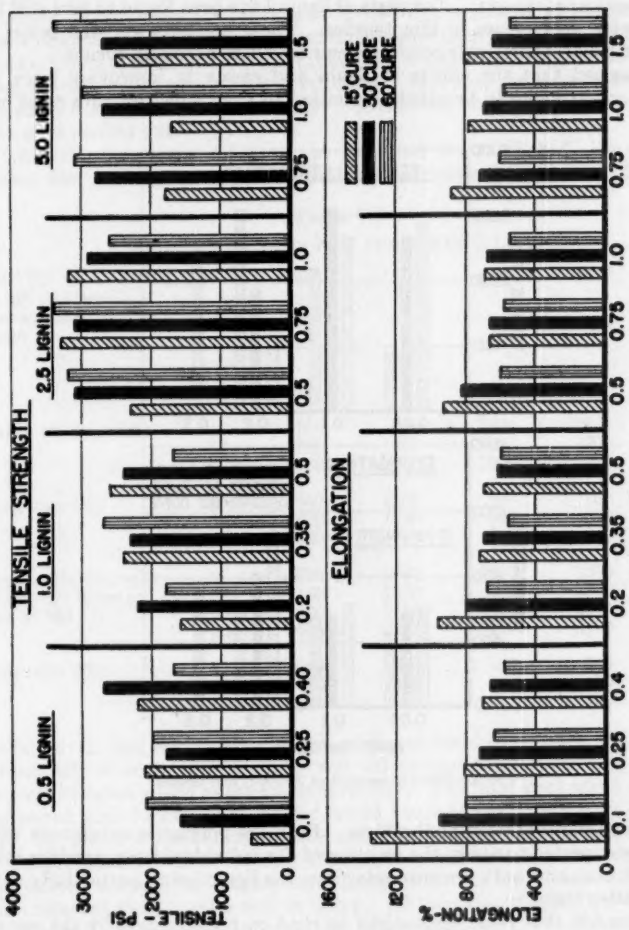


FIG. 5.—Effect of lignin on J-5000-C film tensiles.

presence of casein, but the thickening action of the latter makes its investigation over a range of concentrations difficult. Figure 5 shows film tensiles obtained from J-5000-C latex with amounts of lignin from 0 to 5 parts at several accelerator levels. The marked effect of the lignin on both cure rate and film tensiles is evident. About 2.5 parts of lignin appear to be optimum, with 5 parts giving no further improvement. Ten parts of lignin have been found to give stiff logy stocks with no increase in film tensiles. These amounts are well below the levels at which appreciable reinforcement by fillers normally occurs.

It seemed that the effects of lignin and casein in improving latex film tensiles might logically be attributed either to their effect on cure rates or to

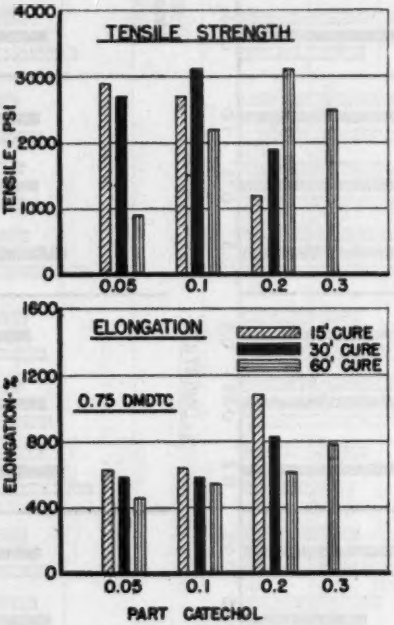


FIG. 6.—Effect of catechol on J-5000-C film tensiles.

mechanical improvement of the films. Both are polymeric substances which might be expected to aid in the knitting of the individual latex particles into a coherent film, and both are cure retarders, the lignin being particularly active in the latter respect.

It was felt that some light might be shed on the situation by the use of a nonpolymeric cure retarder which would not be expected to have any effect on the mechanical properties of the film. Catechol, which is well known as a strong retarder, was selected for study. Figure 6 shows tensile results from a series of films of an alginate-thickened J-5000-C latex compounded with 0.75 part of dimethylammonium dimethyldithiocarbamate as accelerator and varying amounts of catechol. Comparison of the tensiles of this series with those

in Figure 5, where lignin was used, shows that catechol does not have the same effect as lignin in giving high film tensiles over wide variations in cure times, although its retarding effect is strongly evident.

From these data it appears that the effect of lignin is probably not primarily due to its effect on cure rate.

Aging Studies.—As this work was carried out primarily to determine the tensile properties of latex-compounded films rather than to develop formulations for practical applications, no comprehensive studies have been made of the aging characteristics of the vulcanized films. However, because of some data indicating that certain additives gave unusually flat curing curves, a few aging tests were carried out.

The following series of films was prepared from J-5000-C latex: (1) a control film containing only the usual compounding ingredients, (2) a film

TABLE VII

EFFECT OF AGING ON FILM FROM J-5000-C LATEX

DMDTC		0.3	0.3	0.75	1.0	1.5
Na salt of cresyl monosulfide		—	1.5	—	—	—
Lignin		—	—	2.5	5.0	10.0
	Cured at 105°C (min.)					
Tensile (lb./sq. inch)	15	2700	600	2700	2200	1700
	30	2200	1500	2700	2200	2000
	60	1900	2000	2800	3000	2200
Elongation (%)	15	660	1300	640	760	940
	30	600	1020	560	680	830
	60	590	750	520	610	660
Aged tensile (lb./sq. inch) (24 hours in air at 105°C)	15	700	2300	2000	3200	2000
	30	1100	2500	2400	2700	2200
	60	800	2400	2100	2600	2000
	Av.	900	2400	2200	2800	2100
Elongation (%)	15	560	610	480	500	440
	30	590	590	490	470	420
	60	580	560	460	480	440

similar to (1) but also containing 1.5 parts per hundred of latex solids of the sodium salt of cresyl monosulfide, and (3) several films containing varying amounts of lignin added as the ammonium salt. The films were cured normally and tested, and duplicates were aged for 24 hours at 105°C in a circulating air oven, *i.e.*, under normal curing conditions. Table VII shows unaged and aged tensile properties of this series of films. It is evident that the control has deteriorated severely in tensile, while those with the cresyl monosulfide and lignin retained their tensiles well on aging. As the aging was carried out under curing conditions, these results could also be viewed as very flat cure curves; this property may be of considerable technical importance.

In order to obtain data on the rate of cure and aging properties at room temperature, two films were compounded with 2.5 parts of lignin and 0.75 part of dimethylammonium dimethyldithiocarbamate as accelerator. One was cured for 30 minutes at 105°C; the other was not cured. Both films were stored in the laboratory at room temperature with no protection against light,

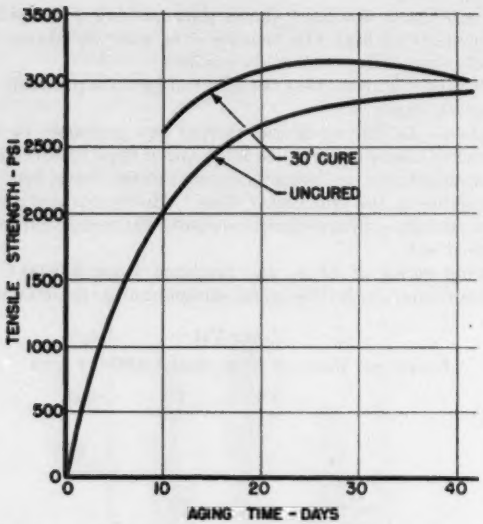


FIG. 7.—Room temperature aging of latex films from J-5000-C latex.

and tensile strips were tested from time to time. Figure 7 shows that curing took place readily at room temperature and that neither film suffered any measurable deterioration in tensile strength within 6 weeks.

Effect of Thickener.—Essentially the same tensile strength was obtained on films from X-635 latex with several different latex thickeners. With J-5000-C and related latexes, however, consistently better results have been obtained with casein than with other thickeners. In order to compare a number of thickeners under similar conditions, a series of films was prepared employing

TABLE VIII

EFFECT OF LATEX THICKNERS ON FILM TENSILES OF J-5000-C LATEX

Thickener[a]		A	B	C	D	E	A	B	C	D	E
Lignin		—	—	—	—	—	2.5	2.5	2.5	2.5	2.5
DMDTC		0.3	0.3	0.3	0.3	0.3	0.75	0.75	0.75	0.75	0.75
	Cured at 105°C (min.)										
Tensile	15	2300	2000	2200	1400	1600	3000	2000	1800	2300	2700
(lb./sq. inch)	30	3200	2400	2600	2000	2500	3400	2800	3200	2500	3200
	60	2000	1200	3000	1100	2300	2700	2100	3700	2700	2500
	Av.	2400	1800	2600	1500	2100	3000	2300	2900	2500	3100
Elongation (%)	15	770	840	820	720	800	660	780	810	720	680
	30	690	710	700	660	730	680	700	680	660	620
	60	600	620	620	580	650	560	540	580	580	520

[a] A. Sodium salt of polyacrylic acid (Acrysol GS, Rohm and Haas Co.).
B. Hydroxyethylcellulose (Cellosize, Carbide and Carbon Chemicals Corp.).
C. Ammonium caseinate.
D. Sodium carboxymethylcellulose (Methocel, Dow Chemical Co.).
E. Salt of alginic acid (Burtonite W, Burton H. Greenwald Co.).

several different thickeners, both with and without the addition of lignin. Data are summarized in Table VIII. From these results it appears that latexes thickened with ammonium caseinate and sodium polyacrylate possess the best tensiles, alginate being only slightly inferior. The other two thickeners gave definitely poorer results both with and without lignin. One high result (the 30-minute cure) with the sodium polyacrylate brought the average up considerably. Over a long series of films the general average with this thickener would probably be somewhat lower than with casein.

TABLE IX

LATEX FILMS FROM PRODUCTION X-683

Date		11/28/51	12/2/51	12/11/51	12/18/51	12/23/51	12/31/51	1/14/52
	Cured at 105°C, (min.)							
Tensile (lb./sq. inch)	15	2800	1800	2400	2500	2400	2500	1800
	30	2300	2300	2800	2900	2600	2800	2500
	60	3200	2200	2500	2300	2100	2700	2200
	Av.	2800	2100	2600	2600	2400	2700	2200
Elongation (%)	15	720	850	720	680	680	660	720
	30	640	700	660	600	610	610	660
	60	580	630	610	560	560	600	600

X-683 AND X-684 LATEX.—In order to check the quality of films obtained from early production of X-683 compared to those from the parent J-5000-C, samples were obtained from storage representing the first seven tank cars of this material produced. They were compounded with a mixed mercaptobenzothiazole-dithiocarbamate accelerator and casein thickener, cured, and tested. Tensile results are summarized in Table IX. It is apparent that the tensiles, although slightly lower than the optimum for J-5000-C, were satisfactory. The average for all cures is 2500 pounds per square inch. These data are expected to be of use in improving the commercial product.

TABLE X

EFFECT OF CREAM REMOVAL ON X-684 FILM TENSILE

Treatment		—	Centrifuged
	Cure (min.)		
Tensile (lb./sq. inch)	15	1600	2700
	30	1800	2900
	60	1900	2700
	Av.	1800	2800
Elongation (%)	15	710	720
	30	620	680
	60	600	620

One sample of X-684 latex was found to give considerably lower film tensiles than J-5000-C or the X-683 samples described above. Inspection showed this sample to contain a considerable amount of the microscopic prefloc as discussed under X-635. Centrifuging this sample and removing the upper layer improved the average film tensiles for three cures from 1800 to 2800 pounds per square

inch (Table X). A photomicrograph of the latex before centrifuging is shown in Figure 3.

MISCELLANEOUS LATEXES.—*Effect of Monomer Ratio.*—GR-S latexes made at high temperatures with about 50/50 ratios of butadiene to styrene give film tensiles considerably higher than those made with 70/30 monomer ratios. In order to determine the effect of monomer ratio on latexes polymerized at low temperatures, films were prepared from J-5248-C, a latex similar to J-5000-C

TABLE XI

FILM TENSILES OF J-5000-C TYPE LATEX WITH 50/50 BUTADIENE-STYRENE
(Sodium polyacrylate thickener)

DMDTC		0.15	0.30	0.45	0.60	0.75	1.0
Indulin A		—	—	—	—	2.5	2.5
	Cured at 105°C, (min.)						
Tensile (lb./sq. inch)	15	1100	1400	1800	1600	1300	1500
	30	1400	1600	2100	2100	2200	2500
	60	1300	1900	2300	3000	2700	2800
Elongation (%)	15	1160	840	760	740	800	820
	30	1120	720	680	640	720	660
	60	780	680	580	590	590	560

but with a 50/50 ratio of butadiene to styrene monomer charge. Table XI shows that the low temperature 50/50 butadiene-styrene latex has about the same tensile properties as the 70/30. Like similar latexes polymerized at higher temperatures, it is considerably slower-curing than latexes containing larger proportions of butadiene. There are some indications that the ultimate in tensile was not reached with the highest accelerator level used in this series.

TABLE XII

EFFECT OF MOONEY VISCOSITY ON LATEX FILM TENSILE
(2.5 parts of lignin, 0.75 DMDTC, sodium polyacrylate thickener)

Latex		J-5613-A	J-5634-A	J-5555-A	J-5000-C
ML-4		25	48	115	164
	Cured at 105°C, (min.)				
Tensile (lb./sq. inch)	15	2000	2400	3200	3000
	30	2400	2600	3000	3400
	60	2700	3000	2400	2700
Elongation (%)	15	1120	680	580	660
	30	800	620	560	570
	60	660	590	490	560

Effect of Mooney Viscosity.—Because of the desirable effects of high Mooney viscosity in polymer for most uses, these low-temperature latexes are normally produced at Mooney viscosities of 150–175 ML-4. In order to determine whether this property affected film tensiles, a series of latexes ranging from 25 to 160 ML-4 was studied. It was found that, although the lower viscosity polymers cured somewhat more slowly, the film tensile underwent little change over this wide variation in plasticity. There did appear to be a slight decrease

in film tensiles at the lowest viscosities. Data are summarized in Table XII.

Dazad-Free Latex.—A Daxad-free latex (J-5441-9) with 4 parts of rosin-acid soap and 1 part of fatty-acid soap as emulsifier per 100 of charged monomers gave tensile results similar to J-5000-C. Film color was considerably improved.

SUMMARY

Studies were made of the influence of a number of polymerization variables on the tensile strength of vulcanized evaporated films from low-temperature high-solids GR-S latexes. Previous reports of film tensiles on the order of 3000 pounds per square inch for latexes of 70/30 butadiene-styrene charge ratio were confirmed. The levels of accelerator necessary for optimum vulcanized properties were found to be considerably lower than those normally used, particularly for latexes shortstopped with dithiocarbamate salts. Microscopic coagulum found in some latex samples had a pronounced effect in decreasing film tensile of vulcanizates. Cured films from latexes emulsified with mixtures of fatty acid and rosin soap possessed considerably better tensile strengths than those from latexes using all fatty acid soap emulsification. Wide variations on Mooney viscosity had relatively little effect on ultimate film tensiles. Incorporation of small amounts of lignin into the latex as the ammonium or sodium salt decreased cure rates of films and aided in giving more reproducible tensile results. Both lignin and the sodium salt of cresyl monosulfide improved the aging characteristics of films.

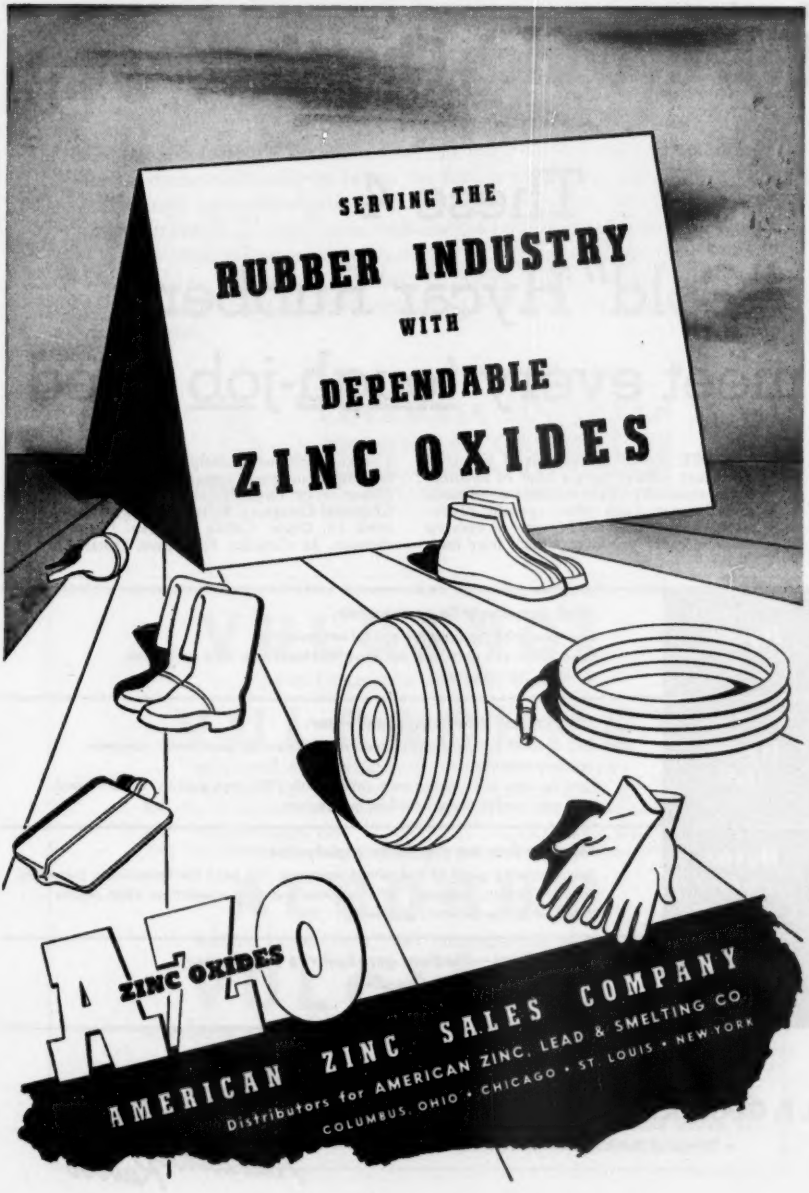
ACKNOWLEDGMENT

This work was carried out under the sponsorship of the Office of Synthetic Rubber of the Reconstruction Finance Corp. in connection with the government's synthetic rubber program. The authors wish to thank that agency for permission to release this publication.

The authors also wish to express their appreciation to John W. Zayatz who prepared and tested all of the latex films and to Harold G. Werner of the Development Department for his cooperation in supplying latex samples. Thanks are also due to James A. Reynolds for preparing the graphs and to C. R. Peaker for helpful advice and criticism.

REFERENCES

[1] Flint, "Chemistry and Technology of Rubber Latex", Van Nostrand & Co., New York, 1938.
[2] Wohler, *India Rubber World* **116**, 66 (1947); Pierson, Coleman, Rogers, Peabody, and D'Ianni, *Ind. Eng. Chem.* **44**, 769 (1952); Talalay and Talalay, *Ind. Eng. Chem.* **44**, 791 (1952).
[3] Wohler, *India Rubber World* **116**, 66 (1947); Talalay and Talalay, *Ind. Eng. Chem.* **44**, 791 (1952).
[4] Smith, Werner, Madigan, and Howland, *Ind. Eng. Chem.* **41**, 1584 (1949).
[5] Smith, Werner, Madigan, and Howland, *Ind. Eng. Chem.* **41**, 1584 (1949); Smith, Werner, Westerhoff, and Howland, *Ind. Eng. Chem.* **43**, 212 (1951); Howland, Neklukin, Brown, and Werner, *Ind. Eng. Chem.* **44**, 762 (1952).
[6] Talalay and Talalay, *Ind. Eng. Chem.* **44**, 791 (1952).
[7] Smith, Werner, Madigan, and Howland, *Ind. Eng. Chem.* **41**, 1584 (1949); Pierson, Coleman, Rogers, Peabody, and D'Ianni, *Ind. Eng. Chem.* **44**, 769 (1952).
[8] Peaker, *Rubber Age* (N. Y.) **57**, 423 (1945).
[9] Brass and Slovin, *Anal. Chem.* **20**, 172 (1948).


SERVING THE
RUBBER INDUSTRY
WITH
DEPENDABLE
ZINC OXIDES
AZO
ZINC OXIDES
AMERICAN ZINC SALES COMPANY
Distributors for AMERICAN ZINC, LEAD & SMELTING CO.
COLUMBUS, OHIO • CHICAGO • ST. LOUIS • NEW YORK

News about

B. F. Goodrich Chemical *raw materials*

These 4 "Cold" Hycar Rubbers meet every tough-job need

THESE "cold" polymerized types of Hycar rubber have a host of applications, especially where toughest conditions must be met. Each offers specific advantages, that can help you improve or develop more saleable products. Check over each one, and write us for helpful technical information on your specific requirements. Please write Dept. HA-1, B. F. Goodrich Chemical Company, Rose Building, Cleveland 15, Ohio. Cable address: Goodchemco. In Canada: Kitchener, Ontario.

Hycar 1041	***High acrylonitrile copolymer.*** Easy processing, excellent oil and solvent resistance. Used for oil well parts, fuel cell liners, fuel hose, rolls, lathe cut gaskets, packings, "O" rings, etc.
Hycar 1042	***Medium acrylonitrile copolymer.*** Easy processing, very good oil and solvent resistance, good water resistance, excellent solubility Used for shoe soles, kitchen mats, printing rolls, "O" rings, gaskets, etc. GR-S and vinyl resin modifications, adhesives and cements.
Hycar 1043	***Medium low acrylonitrile copolymer.*** Easy processing, good oil and solvent resistance, very good low temperature properties. Used for gaskets, grommets, "O" rings, hose and other applications which require improved low temperature properties.
Hycar 1432	***Crumb form—Medium acrylonitrile copolymer.*** Directly soluble—no milling required. Used for cements and adhesives.

B. F. Goodrich Chemical Company

A Division of The B. F. Goodrich Company

Hycar American Rubber

GEON polyvinyl materials • HYCAR American rubber • GOOD-RITE chemicals and plasticizers • HARMON colors

NEW SILENE DATA BULLETIN

Columbia-Southern's Technical Staff has just reviewed the compounding formulations and results of Silene, the rubber reinforcing pigment.

The new up-to-the-minute data has been compiled into 31 compact pages, in handy 6" x 9½" size, with margin perforations for easy binding.

This factual information is invaluable to anyone seeking a good non-black rubber reinforcing pigment. If rubber compounding is in your picture, write today on your company's letterhead for this new Silene data bulletin.

COLUMBIA-SOUTHERN CHEMICAL CORPORATION
SUBSIDIARY OF PITTSBURGH PLATE GLASS COMPANY
ONE GATEWAY CENTER, PITTSBURGH 22, PENNSYLVANIA

VULCANOL®

Latex Compounds of Proven Quality

VULCACURE®

AQUEOUS SUSPENSIONS OF ULTRA ACCELERATORS

VULCACURE ZM
50% Zinc Dimethyldithiocarbamate

VULCACURE ZE
50% Zinc Diethyldithiocarbamate

VULCACURE ZB
50% Zinc Dibutyldithiocarbamate

VULCACURE NB
47% Sodium Dibutyldithiocarbamate

ALCOGUM

Sodium Polyacrylate Latex Thickener and Stabilizer

VULCARITE®

A Series of Water Dispersions of Latex Compounding Chemicals

•

Technical information and samples available promptly upon request.

ALCO OIL & CHEMICAL CORP. Trenton Ave. and William St. Philadelphia 34, Pa.

The C.P. Hall Co.
CHEMICAL MANUFACTURERS

ACCELERATORS
PLASTICIZERS
ANTIOXIDANTS

A Complete Line of Approved Compounding Materials

● AKRON, OHIO • LOS ANGELES, CALIF. • CHICAGO, ILL. • NEWARK, N. J.

STAMFORD "FACTICE"
VULCANIZED OIL

(Reg. U. S. Pat. Off.)

Our products are engineered to fill every need in natural and synthetic rubber compounding wherever the use of vulcanized oil is indicated.

We point with pride to a complete line of solid Brown, White, "Neophax" and "Amberex" grades, and hydrocarbon solutions of "Factice" for use in their appropriate compounds.

Continuing research and development in our laboratory and rigid production control has made us the leader in this field.

The services of our laboratory are at your disposal in solving your compounding problems.

THE STAMFORD RUBBER SUPPLY COMPANY
STAMFORD, CONNECTICUT

Manufacturers of "Factice" Brand Vulcanized Oil Since 1900

Now Available—

1953-54 Edition of

RUBBER RED BOOK

Directory of the Rubber Industry

Ninth Issue — 1200 Pages

Completely Revised and Up-to-Date

PRICE: $10.00* Postpaid in All Countries

Second Edition of

LATEX in INDUSTRY

By ROYCE J. NOBLE, Ph.D.

912 Pages • 6 x 9 Inches • 25 Chapters
Bibliography • Author Index • Subject Index

PRICE: $15.00* Postpaid in U. S.
$16.00 Postpaid in All Other Countries

(*) Add 3% Sales Tax for Copies to New York City Addresses

Published by

RUBBER AGE

250 West 57th St. New York 19, N. Y.

STOP RISING COSTS

with

Piccolyte

the versatile resin

Costs Less...Offers More!

Piccolyte—a pure hydrocarbon, thermoplastic terpene resin—is low in cost and readily soluble in low-cost naphthas, pentane and hexane. It is pale and stable in color, chemically inert, compatible with many other materials, non-toxic. There are nine melting points.

Piccolyte has the same carbon to hydrogen ratio as plantation rubber, and has excellent tack-producing properties. Ideal for rubber tile and other products where light colors and tints are demanded.

Use Piccolyte to keep your costs down without sacrificing in any way the quality of your products. Piccolyte costs less per pound today than practically all other resins, yet offers the maximum in quality and service.

Write for data booklet, and a free sample of PICCOLYTE. Give intended use, so we can send sample of appropriate grade.

PENNSYLVANIA
INDUSTRIAL CHEMICAL CORP.
CLAIRTON, PA.
Plants at Clairton, Pa. and Chester, Pa.
Distributed by Harwick Standard Chemical Co., Akron 5, Ohio

Ready Now!

MACHINERY and EQUIPMENT for RUBBER and PLASTICS

VOLUME I
PRIMARY MACHINERY AND EQUIPMENT

The only book of its kind ever offered to the Rubber and Plastics Industries and the first to be published since Pearson's "Rubber Machinery" in 1915. Compiled by Robert G. Seaman and Arthur M. Merrill, the present Editors of India RUBBER WORLD, with the cooperation of an Editorial Advisory Board of experts in their respective fields. Each chapter is preceded by an article written by recognized authorities on the equipment, its purposes for specific products, and best method of using it.

Volume I has over 800 pages of editorial content with authoritative descriptions for each machine classification: Types, Specifications, Design Features, Operation, and Applications, as well as names and addresses of the manufacturers or suppliers. More than 300 illustrations. Cloth-bound for permanence.

Send for free copy of complete prospectus.

Volume I—$15.00 Postpaid in U. S. A.
$16.00 Elsewhere

Volume II—Supplementary Machinery and Equipment, is now in preparation and will be published in the near future.

INDIA
RUBBER WORLD
386 FOURTH AVENUE NEW YORK 16, N. Y.

ST. JOSEPH LEAD COMPANY
ST. JOE
ZINC OXIDE
JOSEPHTOWN, PA.

ST. JOE *lead-free* ZINC OXIDES

a Grade for Every Purpose

Our unique electrothermic smelting method, the latest improvement in the production of zinc oxide by the American Process, ensures the uniformity of these St. Joe pigments because of the close control exercised at the most critical point — *the instant of oxidation.* This control applies to both chemical composition and particle size, and is largely responsible for the preference accorded our products by a steadily increasing number of zinc oxide consumers.

ST. JOSEPH LEAD COMPANY
250 PARK AVENUE, NEW YORK 17, N Y
Plant & Laboratory: Josephtown, Beaver County, Pa.

ANTIMONY SULPHIDE

Regular Grades *for* Attractive Color

Also

A special grade for obtaining colored stocks having high abrasion resistance

RARE METAL PRODUCTS CO. **ATGLEN, PENNA.**

SUPERIOR ZINC CORPORATION

121 North Broad Street Philadelphia 7, Penna.

Works at Bristol, Pa.

RUBBER SUBSTITUTES

(Vulcanized Vegetable Oils)

Manufactured since 1903 by

THE CARTER BELL MFG. CO.

SPRINGFIELD NEW JERSEY

Represented by:

HARWICK STANDARD CHEMICAL CO.

Akron — Boston — Trenton — Chicago — Denver — Los Angeles

Last year it was:

Do YOU belong to the FOUR HUNDRED?

...odel NBS Mooney Viscometers have been manufactured and distributed by us since 1943. These are in world wide use. This universal acceptance is based upon their proven value as a control in the production of synthetic rubbers and in the grading of Technically Classified Natural Rubbers. In the manufacture of rubber products, the Mooney Viscometer has greatly improved the control of processibility. It has also been found invaluable for rapid and accurate determinations of the relative rates of Scorch and Cure characteristics of compounded materials.

NOW by the end of 1953 it's over FIVE HUNDRED

Rapidly increasing adoption of the Scott-NBS Mooney Viscometer has brought the total to

more than 500

in world-wide use by the Rubber Industry for rapid and accurate determination of Scorch and Cure characteristics.

REQUEST "NBS LITERATURE"

SCOTT TESTERS, INC. 102 Blackstone St. Providence, R. I.

Scott Testers — Standard of the World

WHITETEX

A new white and bright pigment for rubber, synthetic rubber or plastics, especially vinyls.

BUCA

A proved pigment for compounding ALL types of natural and synthetic rubber.

CATALPO

For compounding rubber and synthetic rubber.

No. 33 CLAY

For wire and vinyl compounding.

●

For full details, write our Technical Service Dept.

SOUTHERN CLAYS, INC.

(Formerly P. W. Martin Gordon Clays, Inc.)

33 Rector Street • New York 6, N.Y.

CARBON BLACKS

Wyex (EPC)
Easy Processing Channel Black

Arrow TX (MPC)
Medium Processing Channel Black

Essex (SRF)
Semi-Reinforcing Furnace Black

Modulex (HMF)
High Modulus Furnace Black

Aromex (HAF)
High Abrasion Furnace Black

Aromex 115 (CF)
Conductive Furnace Black

Aromex 125 (SAF)
Super Abrasion Furnace Black

Arovel (FEF)
Fast Extruding Furnace Black

Collocarb
80% Carbon Black + 20% Process Oil

CLAYS

Suprex Clay . . . . High Reinforcement
Paragon Clay . . . . . Easy Processing
Hi-White R . . . . . White Color

RUBBER CHEMICALS

Turgum S, Natac, Butac . . . . . Resin-Acid Softeners
Aktone . . . . . Accelerator Activator
Zeolex 20 . . . . . Reinforcing White Pigment

HUBER J. M. HUBER CORPORATION • 100 Park Ave., New York 17, New York

consult **TITANOX** *technical service department*

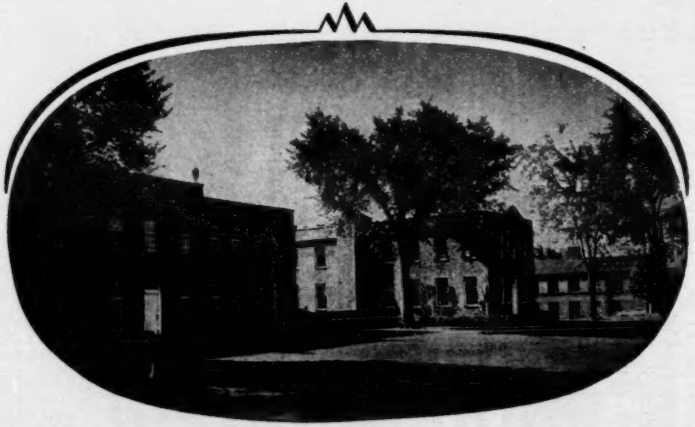
for assistance with your white pigmentation problems

1880

TITANIUM PIGMENT CORPORATION

Subsidiary of **NATIONAL LEAD COMPANY**

TITANOX
the brightest name in pigments



THE VANDERBILT MODEL LABORATORY

NORWALK, CONNECTICUT

Here we learn how our materials can be used by our customers to their best advantage. We invite and appreciate your cooperation.

Please feel free to visit our laboratory, to discuss your problems with us and to use our facilities to work them out if you care to do so.

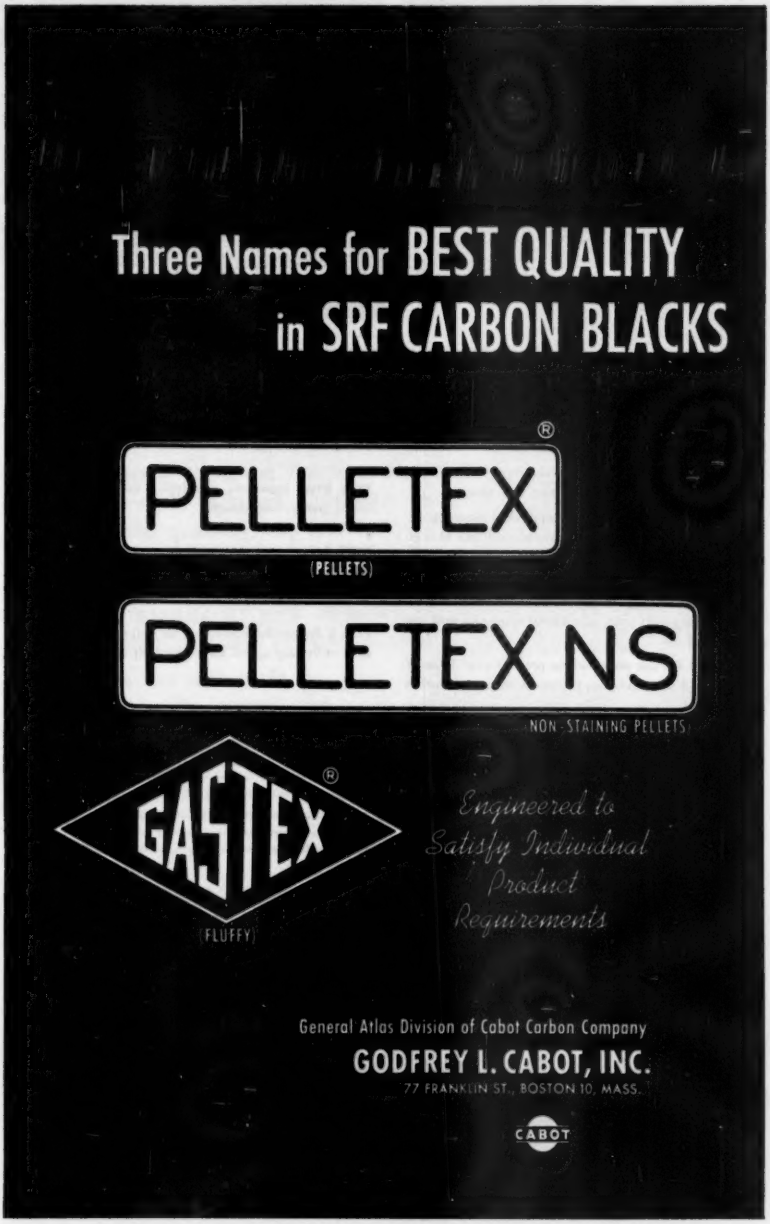
R. T. VANDERBILT CO., INC.

230 Park Avenue, New York City

RUBBER CHEMISTRY AND TECHNOLOGY IS SUPPORTED BY ADVERTISING FROM THESE LEADING SUPPLIERS

INDEX TO ADVERTISERS

	Page
Alco Oil and Chemical Corp.	19
American Cyanamid Company, Calco Chemical Division	11
American Zinc Sales Company	17
Binney & Smith Company...(Opposite Table of Contents)	16
Cabot, Godfrey L., Inc.	9
Carter Bell Manufacturing Company, The	25
Columbia Southern Chemical Corp.	19
Du Pont Rubber Chemicals Division	32
General Atlas Carbon Company	31
Goodrich, B. F., Chemical Company	18
Goodyear Tire & Rubber Company, The	5
Hall, C. P. Company, The	20
Harwick Standard Chemical Company (Inside Back Cover)	
Huber, J. M., Corporation	28
India Rubber World	23
Koppers Company, Inc. (Chemical Division)	10
Monsanto Chemical Company	6
Naugatuck Chemical Division (U. S. Rubber Company)	13
Neville Chemical Company	12
New Jersey Zinc Company, The (Outside Back Cover)	
Pan-American Refining Corp., Pan American Chemicals Div.	8
Pennsylvania Industrial Chemical Corp.	22
Phillips Chemical Company	2
Rare Metal Products Company	25
Richardson, Sid Carbon Company	7
Rubber Age, The	21
St. Joseph Lead Company	24
Scott Testers, Inc	26
Sharples Chemicals, Inc.	3
Southern Clays, Inc.	27
Stamford Rubber Supply Company, The	20
Sun Oil Company, Sun Petroleum Products (Opposite Title Page)	14
Superior Zinc Corporation	25
Thiokol Corporation, The	4
Titanium Pigment Corporation	28
United Carbon Company (Inside Front Cover)	
Vanderbilt, R. T. Company	29
Witco Chemical Company...(Opposite Inside Front Cover)	1


Three Names for BEST QUALITY
in SRF CARBON BLACKS
PELLETEX®
(PELLETS)
PELLETEX NS
NON-STAINING PELLETS
GASTEX®
(FLUFFY)
Engineered to
Satisfy Individual
Product
Requirements
General Atlas Division of Cabot Carbon Company
GODFREY L. CABOT, INC.
77 FRANKLIN ST., BOSTON 10, MASS.
CABOT

Performance You Can Rely On!

NEOPRENE

THERE'S A TYPE TO MEET YOUR EXACT REQUIREMENTS

DRY NEOPRENES

GENERAL-PURPOSE TYPES

TYPE GN. Suitable for use in non-staining and light-colored compounds.

TYPE GN-A. Contains a stabilizer that results in improved storage stability; will stain and discolor.

TYPE GRT. Recommended for compounds requiring improved tack retention and maximum resistance to crystallization.

TYPE W. Possesses outstanding storage stability and excellent processing characteristics. Produces vulcanizates having light color, good heat resistance and low permanent set.

TYPE WRT. For use wherever the properties of Type W are desired plus maximum resistance to crystallization.

SPECIAL-PURPOSE TYPES

TYPE AC. Especially developed for quick-setting adhesive cements. Superior in stability and color.

TYPE KNR. Especially developed for high-solids cements, putties and doughs.

TYPE Q. For maximum resistance to oils, chemicals and solvents, particularly EP lubricants, refrigerants and nonflammable hydraulic fluids.

TYPE S. Especially developed for crepe soles. Also used as a stiffening agent for processing other neoprenes.

NEOPRENE LATICES

TYPE 571 (Solids 50%±1%)—General-purpose type for most applications.

TYPE 572 (Solids 50%±1%)—Fast-setting, high wet-strength type for adhesives.

TYPE 601A (Solids 59%±1%)—For dipped and coated goods and for foam. Improved resistance to crystallization.

TYPE 735 (Solids 35%±1%)—A sol type latex. Specially suited for paper making. Used with other latices to improve wet gel strength and extensibility.

TYPE 842A (Solids 50%±1%)—General-purpose, fast-curing type; vulcanizates have improved resistance to crystallization. Recommended for dipping, saturation, and as a binder for fibers.

NEOPRENE RESISTS:
Oxidation • Heat • Sunlight • Ozone • Oils • Grease • Chemicals • Aging • Abrasion • Flame • Flex-Cracking.

JUST PUBLISHED—"The Neoprenes." Here's a 250-page book on the principles of compounding and processing all types of dry neoprene. It's free for the asking. Your Du Pont representative will be glad to secure a copy for you. Just write or phone the nearest Rubber Chemicals district office.

DISTRICT OFFICES:

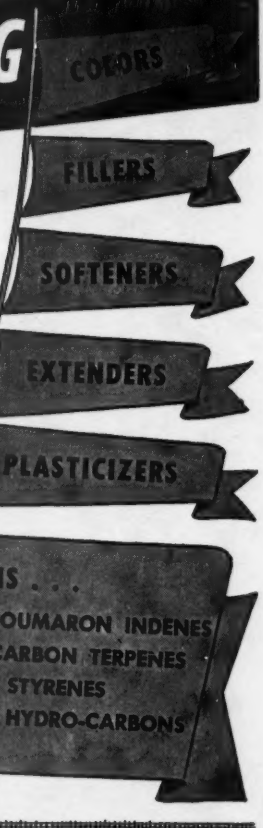
Akron 8, Ohio, 40 E. Buchtel Ave. . . . . Hemlock 3161
Atlanta, Ga., 1261 Spring St., N.W. . . . . Emerson 5391
Boston 5, Mass., 140 Federal St. . . . . Hancock 6-1711
Chicago 3, Ill., 7 S. Dearborn St. . . . . ANdover 3-7000
Houston, Texas, 4141 Dumble St. . . . . ATwood 4566
Los Angeles 58, Cal., 2930 E. 44th St. . . . . LOgan 5-6464
New York 13, N. Y., 40 Worth St. . . . . COrtlandt 7-3966
Wilmington 98, Del., 1007 Market St. . . . . Win. 4-5131

DU PONT RUBBER CHEMICALS

DU PONT

BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY

Material for ALL RUBBER and PLASTIC COMPOUNDING



PRECISION Uniformity

You can depend upon the *Precision* character of Harwick Standard Chemicals regardless of the quantity requirement . . . Here is dependable assurance of uniformity in any type compounding material for rubber and plastics to give *certainty* in product development and production runs.

Our services are offered in cooperative research toward the application of any compounding material in our line to your production problems.

HARWICK STANDARD CHEMICAL CO.

AKRON 5, OHIO

BRANCHES: BOSTON, TRENTON, CHICAGO, LOS ANGELES

You can formulate *FASTER... BETTER* with

HORSE HEAD® ZINC OXIDES

FORMULATE *FASTER!*

...Because the Horse Head line comprises the most complete family of Zinc Oxides for rubber:

1. It is the only line having such a wide range of particle sizes, surface conditions and chemical compositions.
2. Its *conventional* types cover the range of American and French Process oxides.
3. Its *exclusive* types include the well-known Kadox and Protox brands.

That means you need not waste time adapting a single Zinc Oxide to each specific compound. Instead, just choose from the Horse Head line the Zinc Oxides that best meet your needs.

FORMULATE *BETTER!*

...Because you need to compromise less when you choose from the wide variety of Horse Head Zinc Oxides.

...Because the Horse Head brands can improve the properties of your compounds.

Year after year, for nearly a century, more rubber manufacturers have used more tons of Horse Head Zinc Oxides than of any other brands.

THE NEW JERSEY ZINC COMPANY

Founded 1848

160 Front Street, New York 38, N. Y.